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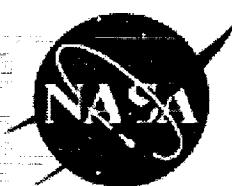
NASA's Upper Atmosphere Research Program (UARP) and Atmospheric Chemistry Modeling and Analysis Program (ACMAP)

March 2000

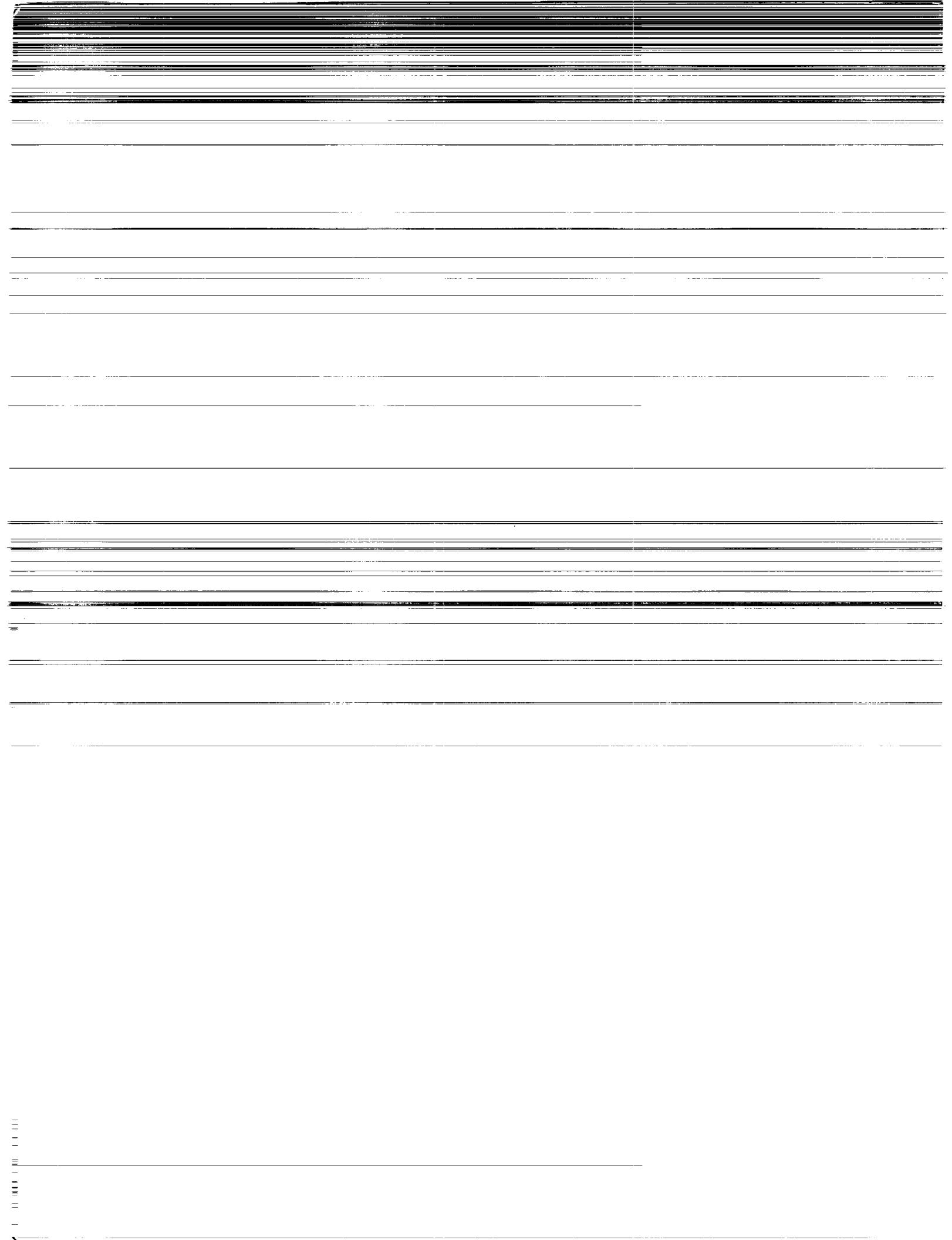
RESEARCH SUMMARIES

1997 - 1999

*Report to Congress
and the Environmental
Protection Agency*



National Aeronautics and
Space Administration
Washington, DC 20546



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TABLE OF CONTENTS

INTRODUCTION	1	
FIELD MEASUREMENTS	7	
A. Balloon-Borne <i>In Situ</i> Measurements	9	
Balloon-Borne <i>In Situ</i> LACE Instrument	J. Elkins/NOAA CMDL	11
Dynamical Studies with the Argus Lightweight Tracer Instrument	M. Loewenstein H. Jost/NASA ARC	14
Balloon-Borne <i>In Situ</i> Ozone Measurements	J. Margitan/JPL	16
Water-Vapor Measurements of the Middle Stratosphere Using a Balloon-Borne Frost-Point Hygrometer	S. Oltmans/NOAA AL	20
ECC Ozonesonde Calibration and Launch	F. Schmidlin/NASA GSFC	22
Balloon-Borne <i>In Situ</i> ALIAS II Instrument	C. Webster/JPL	24
Balloon-Borne <i>In Situ</i> CO ₂ Measurements	S. Wofsy/Harvard U	26
B. Balloon-Borne Remote Measurements	29	
Infrared Measurements of Atmospheric Constituents - Balloon Borne Measurements	F. Murcray/U Denver	31
Far Infrared Measurements of Trace Gases	I. Nolt/NASA LaRC	33
Far IR Radiometer for OH	H. Pickett/JPL	35
Multisensor Measurements	O. Raper/JPL	38
Millimeter and Submillimeterwave Radiometry	R. Stachnik/JPL	40
Stratospheric Fourier Spectrometry	G. Toon/JPL	42
Measurements of HO ₂ and Other Trace Species in the Stratosphere Using a High-Resolution Far-Infrared Spectrometer	W. Traub K. Chance/SAO	45

C. Ground-Based Measurements		49
Latitudinal Tropospheric Concentration Distributions of Selected Halocarbons and Hydrocarbons	D. Blake/UC Irvine	51
Infrared Fourier Transform Spectroscopy in Support of the Network for the Detection of Stratospheric Change (NDSC)	M. Coffey W. Mankin/NCAR	54
Stratospheric and Mesospheric Trace Gas Studies Using Ground-Based Millimeter Wave Receivers	R. de Zafra/SUNY	56
Support for NASA-Sponsored Research Projects, Including the Network for the Detection of Stratospheric Change, at Mauna Loa and American Samoa	D. Hofmann/NOAA CMDL	59
NDSC Ozone Lidar and Instrument Support	I. McDermid/JPL	61
NDSC Mobile Lidar	T. McGee/NASA GSFC	65
Measurements of Hydroxyl Column Abundances	K. Minschwaner/NM Tech	68
Infrared Measurements of Atmospheric Constituents - Ground Based Observations	F. Murcray/U Denver	70
Ground Based Monitoring of Water Vapor in the Earth's Middle Atmosphere	R. Nedoluha/NRL	73
NDSC Microwave Ozone Instruments	A. Parrish/U Mass	76
Advanced Global Atmospheric Gases Experiment (AGAGE)	R. Prinn/MIT R. Weiss/SAO	79
UV/Visible Interferometry	S. Sander/JPL	83
NDSC ClO Instrument	P. Solomon/SUNY	86

D. Aircraft-Borne Measurements		89
Airborne Measurements of Aerosol Parameters and Trace Gas Species	B. Anderson/NASA LaRC	91
Clouds and Water Vapor in the Climate System	J. Anderson/Harvard U	92
<i>In Situ</i> Detection of OH, HO ₂ , ClO, BrO, NO ₂ , ClONO ₂ , H ₂ O and O ₃ from the ER-2	J. Anderson/Harvard U	95
Trace Gas Measurements for Whole-Air Sampling	E. Atlas/NCAR	101
Measurements of Aerosol and Cloud Particles	D. Baumgardner B. Gandrud/NCAR	105
Stratospheric Chemistry and Transport Through Isotopic Analyses of Trace Gases	K. Boering/UC Berkeley	107
Measurements of Particle Size Distributions in the 4 to 2000 nm Diameter Range	C. Brock/U Denver	111
Airborne Lidar Stratospheric Ozone, Water Vapor, and Aerosol Investigations	E. Browell/NASA LaRC	112
DC-8 Measurements of ClO, BrO, and HO _x	W. Brune/Penn State	115
ER-2 Meteorological Measuring System (MMS)	P. Bui/NASA ARC	117
Airborne Raman Lidar	J. Burris T. McGee/NASA GSFC	119
Airborne Infrared Fourier Transform Spectroscopy	M. Coffey W. Mankin/NCAR	121
Airborne Trace Gas Measurements	J. Elkins/NOAA CMDL	123
Reactive Nitrogen Measurements on the ER-2 High Altitude Aircraft	D. Fahey/NOAA AL	127
Diode Laser Airborne Water Vapor Measurements	R. Herman/JPL	129

Aircraft Deployment Management	S. Hipskind M. Craig/NASA ARC	131
Stratospheric N ₂ O Tracer Studies with the ATLAS ER-2 Diode Laser Spectrometer	M. Loewenstein J. Podolske/NASA ARC	134
Microwave Temperature Profiler	M. Mahoney/JPL	136
Composition and Photodissociative Flux Measurements	C. McElroy/AES Canada	139
Upper Tropospheric-Lower Stratospheric Aircraft <i>In Situ</i> Ozone Measurements	E. Richard/NOAA AL	142
Differential - Absorption IR Measurements of CO, CO ₂ , CH ₄ , N ₂ O, and H ₂ O _(v)	G. Sachse/NASA LaRC	146
Atmospheric Photolysis Frequency Measurements	R. Shetter/NCAR	149
Physical and Chemical Properties of Aerosols and Cloud Particles: Ames Wire Impactor Applications	A. Strawa/NASA ARC	150
Free Radical Measurements from the DC-8 Aircraft	D. Toohey/U Colorado	153
CIMS Measurements of Atmospheric Nitric Acid	A. Viggiano J. Ballenthin/AFRL	155
Aircraft Measurements of the ALIAS Instrument	C. Webster/JPL	158
NO and NO _y Measurements in Stratosphere	A. Weinheimer/NCAR	161
Development of an Aircraft-Borne Instrument for Measurement of Nitric Acid	P. Wennberg/Cal Tech F. Eisele/NCAR	164
Aerosol Measurements from the ER-2	J. Wilson/U Denver	166
Aircraft CO ₂ Measurements	S. Wofsy/Harvard U	168

E. Rocket-Borne Measurements		171
Rocket Borne Temperature and Wind Measurements	F. Schmidlin/NASA Wallops	173
LABORATORY STUDIES		175
A. Reaction Kinetics and Photochemistry		177
Kinetics and Mechanisms of Atmospheric Photooxidation	R. Carr/U Minnesota	179
Atmospheric Photochemical Kinetics	W. DeMore/JPL	182
Reaction Intermediates and Mechanisms	R. Friedl/JPL	183
Laboratory Studies of Heterogeneous Processes Related to Stratospheric Ozone Depletion	D. Golden L. Iraci/SRI	186
Chemical Kinetics of the Stratosphere	L. Keyser/JPL	188
Photochemical and Kinetic Studies of Stratospheric and Tropospheric Importance	M. Kurylo/NIST	190
Homogeneous and Heterogeneous Processes	M.-T. Leu/JPL	193
Lab Studies of Infrared Optical Constants and Microphysical Properties of Stratospheric Aerosols	R. Miller/U NC	196
Flow Tube Studies of Gas Phase Chemical Processes	M. Molina/MIT	199
Molecular Beam Studies of Stratospheric Photochemistry	M. Okumura/Cal Tech	201
Laboratory Studies of Reactions and Photochemistry of Halogenated Species That Affect Stratospheric Ozone Abundance	A. Ravishankara J. Burkholder/NOAA AL	203
Lab Studies of Tropospheric and Stratospheric Reactions	S. Sander/JPL	207

Reaction Rate and Reaction Product Measurements	L. Stief/NASA GSFC	210
Reactions of the Upper Troposphere and Lower Stratosphere	G. Tyndall J. Orlando/NCAR	212
Laboratory Investigations of Stratospheric and Upper Tropospheric Chemistry	P. Wine/GA Tech	215
Lab Studies of Chemical and Photochemical Processes Relevant to Stratospheric Ozone	M. Zahniser/Aerodyne	218
B. Spectroscopy		221
Quantitative Infrared Spectroscopy of Minor Constituents of the Earth's Atmosphere	C. Chackerian/NASA ARC	223
Tunable Far Infrared Studies	K. Chance/SAO	225
Millimeter and Submillimeter Spectroscopy	E. Cohen/JPL	228
Millimeter and Submillimeter Spectroscopy	F. De Lucia/Ohio State	231
IR Spectroscopic Studies of Atmospheric Molecules	G. Fraser/NIST	234
Calibration Facilities for NASA at SURF II	M. Furst/NIST	237
A Facility for High Resolution Spectroscopy	M. Giampapa/NSO	240
Middle Atmosphere Radiative Transfer	M. Mlynczak/NASA LaRC	246
Analysis of Atmospheric Spectra	C. Rinsland/NASA LaRC	249
Laboratory Far-IR Quantitative Spectroscopy	J. Sirota/UMBC	253
High-Resolution IR Spectroscopy	M. Smith/NASA LaRC	256
New High-Sensitivity Optical Techniques	J. Steinfeld/MIT	259
Infrared Laboratory Spectroscopy	R. Toth/JPL	262
Laboratory Spectroscopic Measurements	P. Varanasi/SUNY	264

MODELING AND DATA ANALYSIS	265	
A. Stratospheric Dynamics and Related Analysis	267	
Transport and Mixing in Stratosphere and Troposphere	K. Bowman/Texas A&M U	269
Advanced Methods for Data Assimilation	S. Cohn/NASA GSFC	272
Dynamical Meteorology of the Tropical and Extratropical Stratosphere	T. Dunkerton/NWRA	275
Parameterization of Gravity Wave Variability	S. Eckermann/NRL	278
Climatological and Dynamical Studies with SAGE Data	M. Hitchman/U Wisconsin	281
Wave Dynamics and Transport in the Stratosphere	J. Holton/U Washington	284
TOMS Validation Using ER-2 and Ground-Based Datasets	S. Lloyd/JHU	287
General Circulation Studies of the Southern Hemisphere Stratosphere	C. Mechoso A. Arakawa/UCLA	290
Temperature Trends from Satellite Data	P. Newman/NASA GSFC	293
Convectively Generated Gravity Waves	L. Pfister/NASA ARC	295
Analysis of Aircraft and Satellite Measurements	R. Pierce/NASA LaRC	297
Large Scale Stratospheric Transport Processes	R. Plumb/MIT	300
Trace Gas Transport in the Troposphere	R. Plumb/MIT	303
Studies of Interannual Stratospheric Variability	W. Randel/NCAR	304
Acquisition of Near-Tropopause Meteorological Data	J. Tenenbaum/SUNY Purchase	307

Transport and Mixing in the Stratosphere and Troposphere from Chemical Tracer Measurements	D. Waugh/JHU	309
Dynamical Coupling of the Troposphere with the Polar Stratosphere	D. Waugh/JHU	311
B. Atmospheric Chemistry Analysis And Related Modeling		313
B1. PREDOMINANTLY STRATOSPHERIC CHEMISTRY		315
Use of POAM III Data in the SOLVE Campaign	R. Bevilacqua/NRL	317
Satellite-Based Stratospheric and Tropospheric Measurements	K. Chance/SAO	319
Modeling of Cloud Microphysics, Heterogeneous Chemistry, and Photochemistry	K. Drdla/NASA ARC	323
Modeling of the Partitioning of Reactive Odd Nitrogen Species	D. Fahey/NOAA AL	324
Algorithm for Future Ozone Limb Profiling Using Limb Scatter Measurements	B. Herman/U Arizona	327
Satellite Data Studies of the Middle Atmosphere	L. Hood/U Arizona	329
Three-Dimensional and Trajectory Chemistry-Transport Modeling for SOLVE	S. Kawa/NASA GSFC	332
TOMS SO ₂ Studies	A. Krueger/NASA GSFC	334
Modeling and Analysis of the Lower Stratospheric Radiation Field	S. Lloyd/JHU	337
Investigation of Photochemical Processes That Control Stratospheric Ozone	H. Michelsen/AER, Inc.	340
Evaluation of Lower Stratosphere SAGE II NO ₂	M. Newchurch/UAH	343

Meteorological Support for Aircraft Missions	P. Newman/NASA GSFC	346
Modeling of Tracers and Meteorological Data	P. Newman/NASA GSFC	347
Analysis of Far Infrared Experiment Data	J. Park/NASA LaRC	349
Meteorological Support for Airborne Missions	L. Pfister/NASA ARC	351
Tracer Evolution at High Latitudes in Winter (SOLVE)	R. Plumb/MIT	354
Impact of Descending Polar Mesospheric NO _x on Stratospheric Ozone	C. Randall/U Colorado	355
Reprocessing of the Nimbus 7 LIMS Data Set	E. Remsberg/NASA LaRC	357
Analysis of Atmospheric Trace Gas Spectra	C. Rinsland/NASA LaRC	359
U.S. Algorithm Development for Canadian ACE Mission	C. Rinsland/NASA LaRC	363
Model Interpretation of Aircraft, Balloon, and Shuttle Data	R. Salawitch/JPL	365
Photochemical Modeling of Field Data	R. Salawitch/JPL	369
Analyses of MkIV DC-8 Aircraft Observations	B. Sen/JPL	373
Reanalysis of Nimbus 4 BUV Data	R. Stolarski/NASA GSFC	375
Near Real-time Assimilation in Support of Flight Planning for the SOLVE Campaign	S. Strahan/NASA GSFC	377
Middle Atmospheric Hydrogen Photochemistry	M. Summers/NRL	379
DC-8 Mission Support and Data Analysis	O. Toon/NASA ARC	381
Mesoscale Exchange of Vortex Air	A. Tuck/NOAA AL	382
Mapping Antarctic Ozone from Visible-Channel Satellite Data	S. Warren/U Washington	384

Development of Ozone Climatology	S. Wofsy M. McElroy/Harvard U	386
Tropospheric and Stratospheric Composition Retrievals Using the Stellar Occultation Technique	J.-H. Yee/JHU APL	389
B2. PREDOMINANTLY TROPOSPHERIC CHEMISTRY		391
Data-Based Climatologies of Chemical Constituents in the Free Troposphere and Lower Stratosphere	G. Brasseur/NCAR	393
Tropospheric Chemistry Studies using GOME and TOMS	K. Chance/SAO	395
Investigation of Tropical Tropospheric Water Vapor	A. Dessler/UMCP	397
Further Studies of Tropospheric Chemistry Using Satellite Data	J. Fishman/NASA LaRC	399
Analysis of ATMOS Upper Tropospheric Trace Gases	M. Gunson/JPL	402
Direct Measurements of Tropospheric Ozone from TOMS Data	R. Hudson/U Maryland	405
Climatology of Tropospheric CO	W. McMillan/UMBC	408
Derivation of Tropospheric Ozone Climatology and Trends from TOMS Data	M. Newchurch/UAH	411
Use of MAPS, GTE, and MLS to Understand the Troposphere	R. Newell/MIT	414
Tropical Tropospheric Ozone from Satellite, Sondes and Airborne Missions: Data Product Development and Analysis	A. Thompson/NASA GSFC	416
Stable Isotopes and Radiocarbon in Atmospheric Methane and its Sources	S. Tyler R. Cicerone/UC Irvine	419
Study of Tropospheric Ozone and UV Reflectivity Using TOMS Data	Y. Yung/Caltech	422

B3. PREDOMINANTLY AEROSOLS AND RADIATION		425
Use of POAM II and SAM II Aerosol Extinction in an Investigation of the Climatology and Morphology of PSCs	R. Bevilacqua/NRL	427
SBUV/2 and SSBUV Irradiance Data Analysis	R. Cebula/Raytheon ITSS	429
GOME Data Analysis	J. Gleason/NASA GSFC	432
Theoretical Studies of Processes Affecting the Stratospheric and Free Tropospheric Aerosols	P. Hamill/SJSU	434
Aerosol Measurements from TOMS	J. Herman/NASA GSFC	436
Antarctic UV Climatology from TOMS	D. Lubin/SIO	439
Aerosol Retrievals from ATMOS Spectra	M. Newchurch/UAH	441
SAGE II Aerosol Studies	L. Poole/NASA LaRC	443
Developing and Validating an Aerosol Model for the Upper Troposphere	A. Tabazadeh/NASA ARC	445
Improved Solar Atlas from ATLAS-3 ATMOS Spectra	G. Toon/JPL	448
Theoretical Investigation of Clouds and Aerosols	O. Toon/U Colorado	450
Stratospheric Aerosol Microphysics and Physical Chemistry	R. Turco/UCLA	453
C. Global Chemical Modeling		459
Modeling of Isotope Fractionation in the Stratosphere	K. Boering/UC Berkeley	461
Three-Dimensional Model with Interactive Biosphere	G. Brasseur/NCAR	463

Impact of Mineral Aerosols and Asian Emissions on the Chemistry of the Troposphere	G. Carmichael/U Iowa	465
Intercontinental Assimilation Modeling of C and N Chemistry Affecting Tropospheric Ozone	R. Chatfield/NASA ARC	468
Anthropogenic and Natural Contributions to Sulfate Aerosol Over the Oceans	M. Chin/Georgia Tech	472
Global Studies of the Sulfur Cycle	C. Chuang/LLNL	474
3-D Chemistry and Transport Model	A. Douglass/NASA GSFC	477
2-D Modeling Studies of the Middle Atmosphere	R. Garcia/NCAR	480
The Use of a 2-D Model for Understanding Past Ozone Downward Trends and Future Ozone Recovery	C. Jackman/NASA GSFC	482
3-D Models of Tropospheric Chemistry	D. Jacob M. McElroy/Harvard U	485
Use of SAGE-II Observations in 2-D Chemistry-Transport Models	M. Ko/AER, Inc.	489
Coupling Processes Between Atmospheric Chemistry and Climate	M. Ko/AER, Inc.	493
Tropospheric Trace Gas Interactions with Aerosols	J. Penner/U Michigan	497
Coupling Atmospheric Circulation and Chemistry	M. Prather/UC Irvine	500
Interpretation of Trace Gas Data	R. Prinn/MIT	503
Systematic Assessment and Analysis of Two-Dimensional Stratospheric Ozone Models	H. Rabitz/Princeton U	506
Global Modeling of Tropospheric Trace Gases	D. Rind/NASA GISS	509

Stratospheric General Circulation Climate Models	D. Rind/NASA GISS	512
Assimilation of Ozone Data for Global Change Studies	R. Rood/UMBC	515
Chemistry-Climate Coupling in a GCM	D. Shindell/Columbia U	517
A Comparison of Observations and GCM Simulations of the Quasi-Decadal Oscillation	D. Shindell/Columbia U	520
Removal Process in the Boundary Layer and the Atmospheric Lifetime of Methyl Bromide	N.-D. Sze/AER, Inc.	522
Use of SAGE II Data to Validate Results from the AER 2-D Aerosol Model	D. Weisenstein/AER, Inc.	524
Assessing the Role of Coupling between Chemistry and Climate	D. Wuebbles/U Illinois	526
Chemistry and Transport in a Multi-Dimensional Model	Y. Yung/Caltech	530
Organic Bromine in the Troposphere	S. Yvon-Lewis/NOAA AOML	533
Assessment, Coordination, and Miscellaneous		537
Ocean Sources and Sinks of Trace Gases	J. Butler/NOAA CMDL	539
Data Survey and Evaluation	W. DeMore/JPL	542
SPARC Data Center	M. Geller/SUNY SB	543
Isotope Fractionation Studies	A. Goldstein/UC Berkeley	545
Chemical Kinetics Data Evaluation Activities	R. Hampson/NIST	547
Meteorological Support Facility and Data Management	S. Hipskind/NASA ARC	549

NIST-JANAF Thermochemical Tables for Species of Importance to Atmospheric Chemistry	R. Huie M. Chase/NIST	551
Development and Maintenance of the GEIA Web Site	P. Middleton/RAND ESPC	553
Biogeochemical Cycling of Halomethanes	R. Oremland/USGS	554

INTRODUCTION

INTRODUCTION

Under the mandate contained in the FY 1976 NASA Authorization Act, the National Aeronautics and Space Administration (NASA) has developed and is implementing a comprehensive program of research, technology development, and monitoring of the Earth's upper atmosphere, with emphasis on the upper troposphere and stratosphere. This program aims at expanding our chemical and physical understanding to permit both the quantitative analysis of current perturbations as well as the assessment of possible future changes in this important region of our environment. It is carried out jointly by the Upper Atmosphere Research Program (UARP) and the Atmospheric Chemistry Modeling and Analysis Program (ACMAP), both managed within the Research Division in the Office of Earth Science at NASA. Significant contributions to this effort have also been provided by the Atmospheric Effects of Aviation Project (AEAP) of NASA's Office of Aero-Space Technology. The long-term objectives of the present program are to perform research to:

- understand the physics, chemistry, and transport processes of the upper troposphere and the stratosphere and their control on the distribution of atmospheric chemical species such as ozone;
- assess possible perturbations to the composition of the atmosphere caused by human activities and natural phenomena (with a specific emphasis on trace gas geographical distributions, sources, and sinks and the role of trace gases in defining the chemical composition of the upper atmosphere);
- understand the processes affecting the distributions of radiatively active species in the atmosphere, and the importance of chemical-radiative-dynamical feedbacks on the meteorology and climatology of the stratosphere and troposphere; and
- understand ozone production, loss, and recovery in an atmosphere with increasing abundances of greenhouse gases.

In compliance with the Clean Air Act Amendments of 1990, Public Law 101-549, NASA has prepared a report on the state of our knowledge of the Earth's upper atmosphere, particularly the stratosphere, and on the progress of UARP and ACMAP. The current report is composed of two parts. Part I summarizes the objectives, status, and accomplishments of the research tasks supported under NASA UARP and ACMAP in a document entitled, *Research Summaries 1997-1999*. Part II is entitled *Present State of Knowledge of the Upper Atmosphere 1999: An Assessment Report*. It consists of (i) the Executive Summary and Chapter Summaries of the World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 44, *Scientific Assessment of Ozone Depletion: 1998* sponsored by NASA, the National Oceanic and Atmospheric Administration (NOAA), the United Nations Environment Program (UNEP), the World Meteorological Organization (WMO), and the European Commission (EC); (ii) a summary of the 1998 Stratospheric Processes and their Role in Climate, SPARC, ozone trends report; (iii) the policymakers summary of the Intergovernmental Panel on Climate Change, IPCC, report on Aviation and the Global Atmosphere; (iv) the executive summary of the NASA Assessment of the Effects of High-Speed Aircraft in the Stratosphere:1998; (v) the executive summary of NASA's Second Workshop on Stratospheric Models and Measurements, M&M II; (vi) the end-of-mission statement for the Photochemistry of Ozone Loss in the Arctic Region in Summer, POLARIS,

aircraft and balloon measurement campaign; and (vii) highlights of the latest of NASA's reviews of chemical and photochemical data for use in stratospheric modeling.

This NASA program supports a variety of research tasks proposed by scientists from the university, government, and industrial research communities. It also sponsors periodic assessments of the state of our knowledge of the stratosphere and its response to specific perturbations such as releases of halocarbons, aircraft effluents, and other potential pollutants, as well as due to natural forcings such as volcanic eruptions. Funding of the research program was approximately \$23M in FY 1999. Substantial advances in our knowledge of the upper atmosphere have been made in each of the major fields of research outlined below.

UARP activities fall into three broad categories: (1) field measurements (employing *in situ* and remote sensing techniques from ground-based, aircraft, balloon, and rocket platforms); (2) laboratory studies (gas-phase and heterogeneous kinetics, photochemistry, thermodynamics, spectroscopy, and calibration standards development); and (3) process study modeling and data analysis. These analyses include data from various major aircraft campaigns such as the Stratosphere Troposphere Exchange Project (STEP); the Airborne Antarctic Ozone Experiment (AAOE); the first and second Airborne Arctic Stratospheric Expeditions (AASE I and II); the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE); the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effect of Stratospheric Aircraft (ASHOE/MAESA); the Tropical Ozone Transport Experiment/Vortex Ozone Transport Experiment (TOTE/VOTE) mission; the Observations of the Middle Stratosphere (OMS) balloon mission; the Stratospheric Tracers of Atmospheric Transport (STRAT) mission, and the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) campaign.

ACMAP primarily supports the analysis and modeling of space-based and sub-orbital data for tropospheric and stratospheric chemistry, as well as for stratospheric dynamics. Multi-dimensional computational models are heavily used for data analysis, as well as in both retrospective and prognostic modeling studies. ACMAP supports the analysis of datasets on several scales, including balloon profiles, ground-based measurements, the extensive set of aircraft measurements noted above, and the full range of space-based measurements made by NASA and other entities. Among the satellite datasets most extensively analyzed by ACMAP and related NASA data analysis efforts are those from the Stratospheric Aerosol and Gas Experiment (SAGE) I and II, the Total Ozone Mapping Spectrometer (TOMS), the Upper Atmosphere Research Satellite (UARS), the Solar Backscatter Ultraviolet (SBUV) instruments, several instruments which flew as part of NASA's Atmospheric Laboratory for Applications and Science (ATLAS) mission series, the Global Ozone Monitoring Experiment (GOME) aboard the European Space Agency's ERS-2 satellite, and the Department of Defense funded Polar Ozone and Aerosols Mission (POAM) and Mid-Course Space Experiment / Ultraviolet and Visible Imagers and Spectrographic Imagers (MSX/UVISI).

A major focus of international concern has been (and continues to be) the assessment of the combined effects of past and present emissions of CFCs; the present and future releases of existing and proposed CFC alternatives such as the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs); continued increases in the atmospheric concentrations of the halons (used as fire suppressants) and methyl bromide (CH_3Br); as well as continued growth in the atmospheric burden of CO_2 , NO_x , and other gases having significant anthropogenic sources such as N_2O and CH_4 . All of these gases play important roles in defining upper atmospheric

composition through chemically induced changes in stratospheric (as well as upper tropospheric) ozone and through alteration of the atmosphere's radiative balance. Hence, a corollary program goal is to understand the role of stratospheric ozone in the radiative heating and dynamics of the atmosphere and, thereby, to assess the importance of chemical-radiative-dynamical feedbacks on the meteorology and climatology of the stratosphere and troposphere.

Many of the trace gases in the hydrogen, nitrogen, and halogen chemical families which participate in the chemistry of ozone have been measured in the stratosphere and more detailed information on their spatial and temporal variations is becoming available. Laboratory studies (particularly in the area of heterogeneous reactions) have strengthened our knowledge of the chemical kinetics of stratospheric components, and have provided improved data on the spectroscopy of atmospheric gases for applications to atmospheric measurements of trace species. Current research funding supports specific investigations dealing with the following topics:

- Determination of the distribution of trace gases in the stratosphere, with emphasis on those species which influence the ozone balance.
- Observations of the global distribution of ozone, its vertical profile, and temporal variations. A key initiative in this area is the continued operation and implementation of the international ground-based remote-sensing measurement Network for the Detection of Stratospheric Change (NDSC).
- Determination of the geographic distribution and strengths of the sources and sinks for compounds of importance to stratospheric chemistry. A strong focus in this area is associated with chlorofluorocarbon alternatives, such as the HCFCs and HFCs.
- Improvements in the understanding of atmospheric dynamics and transport processes both by theory and advanced measurement technology, emphasizing the transport of constituents across atmospheric "boundaries" including those between the stratosphere and troposphere, the wintertime stratospheric polar vortex and mid-latitudes, and the tropical and mid-latitude lower stratosphere.
- Measurements of the ultraviolet solar irradiance and its temporal variations at the top of the atmosphere, and the relationship between ultraviolet radiation received at the Earth's surface as inferred from satellite data and from measurements at the surface.
- Laboratory studies in spectroscopy and photochemical kinetics relevant to the interpretation of atmospheric measurements and to theoretical simulations of the atmosphere.
- Development of more realistic multi-dimensional models of the stratosphere and troposphere.
- Application of 2-D and 3-D stratospheric models to assess the impacts of changing atmospheric composition.
- Evaluation of theoretical models by comparison with atmospheric measurements.
- Development of new technological ideas, techniques, and instruments for use in stratospheric and tropospheric research.

While the material in this report focuses on the work supported by UARP and ACMAP, it should be noted that there is a significant amount of effort carried out by NASA related to atmospheric ozone which is not directly addressed in this report. This includes work supported through the following programs:

- Earth Observing System (EOS) - Both instrument development and theory and data analysis work are supported through this program.
- Mission Operations and Data Analysis (MO&DA) - This includes support for spacecraft operations, data reduction, and science data analysis (i.e., Science Team and Guest Investigator support) for the UARS, SAGE, TOMS, and SBUV instruments.
- Flight Systems - This includes support for the development of instruments to fly aboard US and other spacecraft, including new instruments in the TOMS and SAGE series and several atmospheric chemistry and solar irradiance instruments to be flown as part of NASA's EOS program.

FIELD MEASUREMENTS

- A. BALLOON-BORNE IN SITU MEASUREMENTS**
- B. BALLOON-BORNE REMOTE MEASUREMENTS**
- C. GROUND-BASED MEASUREMENTS**
- D. AIRCRAFT-BORNE MEASUREMENTS**
- E. ROCKET-BORNE MEASUREMENTS**

A. BALLOON-BORNE IN SITU MEASUREMENTS



Balloon-Borne *In Situ* Lightweight Airborne Chromatograph Experiment (LACE) Instrument

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Research Objectives

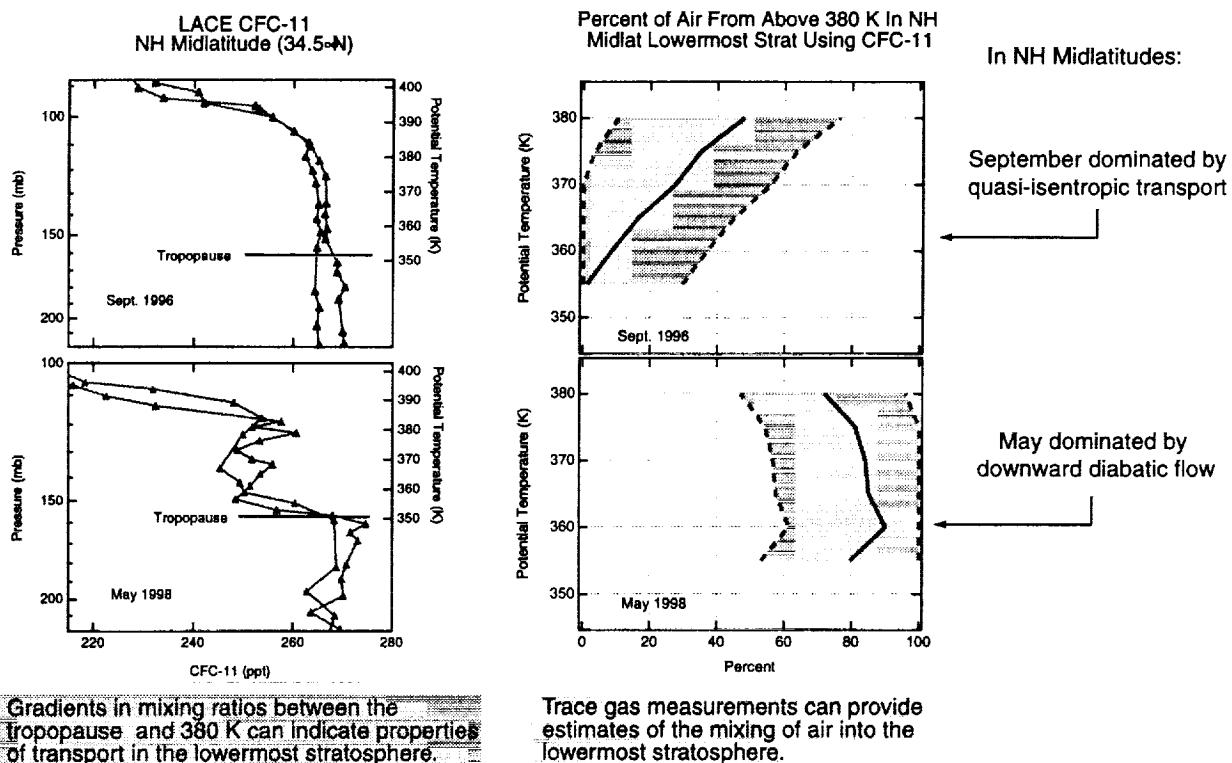
The Lightweight Airborne Chromatograph Experiment (LACE) is designed to measure a variety of organic chlorine, organic bromine, and other trace species in the upper troposphere and lower stratosphere (UT/LS) and middle stratosphere on the JPL balloon gondola for the Observations of the Middle Stratosphere (OMS). More recently LACE was modified for detecting trace gases in the UT/LS on the NASA WB-57 aircraft for Atmospheric Chemistry of Combustion Emissions Near the Tropopause (ACCENT) [Ray *et al.*, 1999]. The main objectives of this research are (1) to measure the trace gases as accurately as possible; (2) study transport through the lowermost stratosphere; (3) determine the hydrogen budget, including CH₄, H₂, and H₂O, in the middle stratosphere; (4) examine tropospheric and mesospheric transport using CO as a tracer, and calculate CO emissions in the air traffic corridors of the U.S.; (5) study stratospheric transport in the tropics; (6) determine the mean age of the air mass; (7) determine the stratospheric lifetimes of the trace gases; and (8) determine the bromine and chlorine budgets of the middle stratosphere.

Summary of Progress and Results

Calibration and Validation (cal-val) of Trace Gases: LACE is similar in design to the Airborne Chromatograph for Atmospheric Trace Species-IV (ACATS-IV) instrument (see Elkins *et al.* [1996], *Geophys. Res. Lett.*, 23 (4), 347-350) operated on the NASA ER-2 aircraft. The key difference is that LACE is housed in a pressurized container and can be operated at sub-ambient pressure for higher altitude sampling (up to 32⁺ km) than the ER-2 aircraft version. The instrument comprises three separate gas chromatographic (GC) channels, each incorporating an electron capture detector (ECD). LACE was configured before the OMS flight (New Mexico, May 18, 1998) with channel 1 for CFC-11, halon-1211, and CFC-12 (70 seconds, 10% OV-101 packed columns), with channel 2 for CFC-11, CFC-113, CHCl₃, CH₃CCl₃, and CCl₄ (140 seconds, 3% OV-101 packed columns), and with channel 3 for SF₆ and N₂O (70 seconds, tri-

columns of Porapak Q/Porapak Q/5 A molecular sieve). LACE was recently modified before the ACCENT mission to measure H₂, CH₄, and CO once every 140 seconds instead of measuring CHCl₃, CH₃CCl₃ and CCl₄. This configuration for the new species will remain on the balloon component of SAGE-3 Ozone Loss Validation Experiment (SOLVE). Measurements from LACE also permit the calculation of the mean age of the air mass, inorganic and organic chlorine, and inorganic and organic bromine. LACE participated in missions from 1996 through 1999, including OMS missions in 1996 through 1998, Stratospheric TRacers for Atmospheric Transport (STRAT) in 1996, Polar Ozone Loss in Arctic Region in Summer (POLARIS) mission in 1997, and the ACCENT mission in September 1999. LACE provides accurate calibration of 9 trace gases because of its frequent calibration (once every 6 injections) where both ambient air and standard are injected at the same pressure and temperature.

Mixing in the Lowermost Stratosphere (Tropopause to 380 K): This region is important because of the large amount of directly deposited aircraft emissions and the potential for circulation changes resulting from climate change to be detected in this region. Scientists from NOAA/CMDL measured vertical profiles of water vapor, CFC-11, halon-1211, SF₆ and other trace gases from a balloon platform during five flights from Ft. Sumner, New Mexico, Juazeiro do Norte, Brazil, and Fairbanks, Alaska [Ray *et al.*, 1999]. These profiles over two seasons were



used to calculate the mixing fraction of air from the overworld (>380 K) into the lowermost stratosphere. Over the midlatitudes, the predominant flow pattern was diabatically downward from the overworld in the spring, while in the fall the flow was quasi-isentropic from the troposphere (see figure above). The transport time of the sampled air from the surface to the lowermost stratosphere was estimated to be less than 1.5 months using the time series of NOAA/CMDL CO₂ and SF₆ ground-based data and stratospheric data from the Harvard CO₂ and LACE instruments.

Bromine and Chlorine Budgets: LACE measures about 50-80% of total organic chlorine in the stratosphere depending on instrument configuration. The missing species, primarily CH₃Cl and HCFC-22, can be estimated by tracer-tracer correlations measured from flask samples taken by the Whole Air Samplers (WAS). Inorganic chlorine can be estimated using the tropospheric trend of the gas and the age of the air mass at the time of entry into the stratosphere from either SF₆ or CO₂ observations (see Woodbridge *et al.* [1995], *J. Geophys. Res.*, 100 (D2), 3057-3064). A similar approach was used for calculating organic and inorganic bromine in the stratosphere (Wamsley *et al.* [1998], *J. Geophys. Res.*, 103 (D1), 1513-1526) since LACE measures about 15% of the total organic bromine, primarily as halon-1211.

Tropical Stratospheric Transport: Balloon measurements have confirmed the earlier results of Volk *et al.* [1996] (*Science*, 272, 1763-1768) on the mixing fraction and entrainment timescale for the partial barrier to transport between the stratospheric extratropics and the tropics. The rate of entrainment and the mixing fraction of midlatitude air in the tropics were estimated by using trace gas measurements from LACE (paper in preparation) and other instruments [Herman *et al.*, 1998] on the NASA OMS balloon gondola. For example, the mixing fraction of midlatitude air in the tropics at 20 km in our study was calculated to about 50% with no statistically significant trend observed on the entrainment rate over altitudes up to 32 km.

Mean Age of the Air Mass: Chemical models tend to underpredict the mean age of the air mass by as high as a factor of 2 compared to balloon-borne results calculated from SF₆ and CO₂ (see Hall *et al.*, *J. Geophys. Res.*, 104 (D15), 18815-18839).

Future Plans: We plan to include shorter lived species, for example, CHCl₃ or CH₃CCl₃, that are more useful for quantifying transport in the UT/LS to LACE with minimal affect to the sampling frequency of the other molecules.

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Dynamical Studies with the Argus Lightweight Tracer Instrument

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Summary of Progress and Results

Argus is a new, two channel, tunable diode laser instrument which measures *in situ* methane (CH_4) and nitrous oxide (N_2O) in the Earth's upper troposphere and stratosphere using the technique of infrared spectroscopic second-harmonic detection. Tracer measurements, that is detection of relatively inert molecules like N_2O and CH_4 , in the atmosphere provide very important information on atmospheric winds and eddies that affect the distribution of ozone and other chemicals in the stratosphere.

Argus was designed and built during the period 1992-1995 and was originally intended to fly on uav (uninhabited aerial vehicle) platforms. It was thus designed to be compact and light as these are small payload vehicles. Because of the rather slow development of the uav for which Argus was designed, the first flight of the instrument took place in 1996 on a stratospheric balloon payload launched from Ft. Sumner, New Mexico. The Argus role in this flight campaign was to profile the tracers, N_2O and CH_4 , to 30 km altitude along with a suite of instruments designed to study dynamics in the stratosphere.

In order to achieve light weight and compactness the Argus instrument uses several different approaches. All optical beams in the laser-to-detector paths are kept as compact as possible by the use of innovative optical design. A detection path of 36 meters for the laser beam passing through the atmospheric sample is achieved in an advanced technology, multi-pass optical cell. This cell, using specially designed and fabricated mirrors, achieves a long multi-pass path in a very small volume. Further innovation in electronics, via the use of surface mount technology, yields a very compact electronic control and data recording stack.

Ethernet communications from a bench computer to the onboard instrument control computer affords extremely versatile instrument setup and testing options. The same communication line provides efficient downloading of very large data files from the on board 85 Mbyte flash memory to our analysis computer. Finally, the data are analyzed using a non-linear least squares (Marquardt-Levenberg) fitting algorithm to convert each 10-second in-flight spectrum into a mixing ratio of N_2O or CH_4 for the 2 instrument channels.

The Argus instrument weighs less than 40 pounds and has dimensions $17 \times 12 \times 9$ inches.

During the period 1996 through 1998 Argus was deployed on balloon launches at several mid- and tropical latitudes. In a launch from Fairbanks, Alaska in late June 1997 the Argus tracer measurements detected two coherent stratospheric air layers which were clearly remnants of the subsided wintertime Arctic vortex. The vortex had broken down several months before this observation and the persistence of the observed layers was a surprise in the vertical profile data from this launch.

During 1997 several balloon launches were carried out in Brazil at 7 S. In this study of tropical stratospheric dynamics at least one new phenomenon was observed by Argus. Several very thin laminae less than 1 km thick of clearly mid-latitude air were observed in the deep tropics at 7 S. These laminae appear to be the signature of air being transported from mid-latitude into the tropics in the middle stratosphere. Such transport has implications for the transport of high flying aircraft exhaust products from the mid-latitudes into the tropical stratospheric ozone production region.

Argus is currently being prepared to participate on the ER 2 aircraft in the SOLVE (SAGE III ozone loss and validation experiment) mission scheduled for January through March in Kiruna, Sweden located at 67 N and lying regularly within the wintertime Arctic vortex.

Publications

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Balloon-Borne *In Situ* Ozone Measurements

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Research Objectives

The research conducted under this RTOP obtains profiles of ozone in the Earth's stratosphere and troposphere using a dual channel UV photometer flown aboard balloons. The high accuracy and precision ozone measurements address a number of objectives, in addition to simply providing ozone profiles: (1) validation measurements are made for other instruments aboard balloons and satellites; (2) measurements at high spatial resolution complement the other predominantly remote sensing instruments; (3) a comprehensive suite of data for testing photochemical models is provided by the combined instruments; and (4) ozone is one of a number of tracer measurements for studying transport. Balloon flights are supported by the JPL Balloon Flight Support Group. In addition, the PI participates as the co-PI for the NOAA Ozone instrument aboard the ER-2 (see the Aircraft Ozone Photometer summary).

Summary of Progress and Results

The major activity during this period has been participation in 8 balloon flights and 4 ER-2 deployments associated with the STRAT and POLARIS campaigns. Observation of the Middle Stratosphere (OMS) balloon flights augmented those predominantly ER-2 campaigns. The Ozone Photometer flew aboard the OMS *in situ* gondola with several other instruments making measurements of tracers at altitudes from the surface to 32 km. Ozone and pressure were measured at high accuracy (3% and 1%, respectively) on all flights, with a time response of 1-second (approximately 15 meters). These tracer measurements extended the datasets obtained by similar instruments aboard the ER-2. During this period 2 flights were performed at midlatitudes in Fall 1996 and Spring 1998, 1 flight from high latitudes in Summer 1997, and 3 flights from the tropics: 1 in February 1997 and 2 in November 1997. Results from these flights have been analyzed to yield information about transport and mixing times in the tropics, and show distinct differences in tracer-tracer correlations (e. g., O₃-N₂O) between the various sites, although not with season. Comparisons of the balloon observations with a variety of 2D models shows differing levels of agreement, suggesting that further analyses can lead to improvements in the models. The Summer 1997 Fairbanks flight encountered 2 layers of air that showed evidence of incomplete mixing of descended, winter vortex air, even at the end of June.

In addition to the *in situ* gondola flights, the Ozone Photometer flew in April 1997 from Fairbanks with the SAO FIRS-2 instrument, the JPL SLS, and an aerosol instrument from the University of Nagoya to provide validation data for the Japanese ADEOS satellite, especially the ILAS instrument. Good agreement was found among the ozone measurements from the photometer, FIRS-2, and ILAS and from nearby ozonesondes, as well as a coincident ER-2 flight. Later that summer, the Ozone Photometer also flew with the JPL MkIV interferometer and Canadian Sun Spectrophotometer.

The goal of POLARIS was to understand the cause of the observed summer decrease in ozone in the Arctic, and synergistically combined balloon and ER-2 platforms to maximize coverage of both latitude and altitude. A comparison of the April and June balloon ozone profiles from Fairbanks showed a decrease in ozone in the summer between 15-25 km that was in good agreement with that calculated based on MkIV measurements of NO_x. During summer, the ER-2 regularly encountered air masses that showed evidence of mixing with vortex fragments, which complicates the attempt to unambiguously derive a signature of ozone loss due to enhanced NO_x photochemistry. Nonetheless, changes in ozone (from the ER-2, balloon ozone photometer, and sondes) were seen between spring and summer that were consistent with those expected. The ozone data also play a critical role in the many photochemical studies carried out with the other measurements aboard the ER-2, especially those involving free radicals and nitrogen partitioning. The ER-2 results are discussed in some detail in the Aircraft Ozone Photometer summary.

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Water Vapor Measurements of the Middle Stratosphere Using a Balloon-Borne Frost-point Hygrometer

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Research Objectives

In order to understand the dynamics and chemistry in the lower and middle stratosphere the Observations of the Middle Stratosphere (OMS) balloon package has been developed. The complement of instruments emphasizes the measurement of atmospheric constituents that provide information on transport processes. A chilled mirror water vapor sensor flown on small balloons that fly with the OMS balloon package is used to measure water vapor and temperature from the troposphere up to about 30 km. Water vapor plays a significant role in the radiative balance and chemistry of this region and is likely increasing as a result of increasing atmospheric methane levels and perhaps as a result of a moister troposphere. In addition the water vapor distribution in the lower stratosphere reflects the processes that exchange material between the troposphere and stratosphere, particularly in the tropics, and is sensitive to the tropopause temperature at which water enters the stratosphere.

Summary of Progress and Results

Water vapor profiles were obtained on balloon flights in conjunction with OMS campaigns in Fort Sumner, New Mexico in September 1996 and May 1998 and Juazeiro do Norte, Brazil in February 1997 and November 1997. It was found in earlier test flights that the best water vapor data is obtained using small balloons flying in coordination with the OMS package. Because the OMS package is designed to descend at relatively slow rates for better height resolution from other sensors, it was found that outgassing of water vapor from the balloon and gondola often contaminated the measurements of water vapor made on the gondola itself. The coordinated small balloon water vapor and temperature measurements could be well integrated with the data from the OMS package.

From the New Mexico flights in September and May an estimate was made of the relative amounts of air in the lowermost stratosphere that are from the troposphere and from the

stratosphere [Ray *et al.*, 1999] for the contrasting seasons. In September about 40% (with wide uncertainty estimates) of the air in the lowermost stratosphere came from the stratosphere above about 15 km. In May, on the other hand, almost 90% of the air in the lowermost stratosphere came from above 15 km. For May this estimate agrees well with that derived using CFC-11. In May, however, the water vapor data suggest that less of the air is from above 15 km at least near the tropopause. The results from the OMS measurements show the usefulness of high resolution, *in situ* measurements of long-lived tracers to help determine the time and spatial scales of transport in the region of the lowermost stratosphere.

The movement of air from the tropical troposphere into the stratosphere can be seen in the upward propagation of the seasonal signal in water vapor concentration over Brazil. The seasonal minimum in the water vapor profile propagates upward approximately 1.5 km from about 18.5 km between February and November 1997. Upward propagation of the maxima in the profiles is also observed.

Publications

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ECC Ozonesonde Calibration and Launch

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Research Objectives

Monitoring the depletion of atmospheric ozone requires that weekly observations of ozone vertical distribution be accomplished from Wallops Island. Daily total-column ozone amounts from a Dobson Spectrophotometer also are provided. Agreement between NASA in the United States and INPE in Brazil calls for additional ozone observations to be made weekly. Observation schedules are flexible so that measurements can be obtained with overpass of NASA research instruments on board various satellites, such as HALOE. Special observational studies leading to improvement of the ozonesonde instrument are conducted periodically. Understanding instrument accuracy and its behavior under variable situations is important to properly represent atmospheric ozone. Comparisons with different balloon-borne instrumentation and remote measurements are to continue.

Summary of Progress and Results

The long term, weekly balloon-borne ozonesonde observation program that began in 1966 continues to provide valuable profiles of ozone distribution necessary for estimating the rate of ozone depletion. Similarly, total-column measurements from the Dobson Spectrophotometer are obtained daily, weather permitting. Dobson measurement data are freely exchanged through World Ozone Data Center located in Toronto. The changes occurring in the total ozone overburden are monitored using these measurements.

Although ozone soundings are conducted weekly, numerous other ozonesonde soundings are timed to coincide with the overpass of satellite remote measuring instruments such as HALOE, SAGE-II, SBUV, and others. Global coverage available from satellites is a key facet of the program for monitoring ozone change, nonetheless, the *in situ* measurements afforded by the balloon-borne ozonesonde is necessary for the continual validation of the remote instruments. Comparisons carried out between the ozonesonde and the ground-based lidar operated by Dr. Tom McGee of Code 916 Goddard Space Flight Center resulted in relatively good agreement considering the time and spatial differences between the test sites. Tests also included the ALOMAR lidar located at the Norwegian range in Andenes.

Specific experimental missions are also conducted with international partners of NASA; e.g., the University of Wuppertal instrument the CRyogenic Infrared Spectrometers and Telescopes for the Atmosphere, or CRISTA. CRISTA was launched from the space shuttle STS-85 and provided measurements of 11 constituents, including ozone, and temperature. The CRISTA instrument remained on orbit for seven days and depended heavily on the ozonesonde for enhancement of the reduction algorithms. International agreements with research groups of different countries, e.g., INPE of Brazil also works with NASA in providing measurements from the INPE facility located at Natal, Brazil, an Equatorial site.

Periodic calibration of the ozonesonde instruments is made against known standards in order to make available valid corroborative data to NASA's remote sensing program. Additionally, comparisons between different instrument types are made to insure that measurement differences that may occur are reconciled. Further, research of ozonesonde instrument behavior is directed toward improving measurements and ultimately the instruments, and as new instruments and improved methods become available tests are conducted and an analysis prepared and distributed.

GPS technology is now available with the standard ozonesonde instruments. When fully implemented more accurate pressure and altitude information will be available as part of the ozone records.

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Balloon-Borne *In Situ* ALIAS-II Instrument

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Research Objectives

The Aircraft Laser Infrared Absorption Spectrometer measurements task has as its primary objective the collection of data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere and troposphere. The *in situ* laser absorption spectrometers ALIAS (ER-2) and ALIAS-II (balloon) provide measurements of several gas concentrations as part of multi-instrument aircraft and balloon payloads flown for NASA missions, and for satellite correlative measurements, e.g., the Upper Atmospheric Research Satellite (UARS) and the Stratospheric Aerosol and Gas Experiment (SAGE III). The instruments use tunable diode lasers in the 3-10- μm wavelength region to measure gas concentrations in multi-pass optical cells either contained in a flow vessel (ALIAS) or in an open-path deployed cradle (ALIAS-II). The instruments have demonstrated capability for N₂O, CH₄, HCl, CO, and NO₂ at the tens-of-parts-per-trillion levels, with capability to measure other gases within the 3-20- μm wavelength region. ALIAS is a 4-channel instrument, ALIAS-II is a 2-channel instrument

Summary of Progress and Results

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS-II) instrument is a lightweight (70 lb.) two-channel version of the ER-2 ALIAS instrument, and was originally built in 1994 specifically for Perseus-type RPV platforms, with an open-path sampling from fuselage to wing. This instrument was modified in 1995 for its participation in the ballooning components of the Stratospheric Tracers of Atmospheric Transport (STRAT) mission of 1995/1996 and the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission of 1997.

In support of the Observations of the Middle Stratosphere (OMS) components of STRAT and POLARIS, the multi-instrument balloon payload that includes ALIAS-II has been flown seven times since 1996, out of Ft. Sumner, New Mexico; Rio del Norte, Brazil; and Fairbanks, Alaska. For all ALIAS-II balloon flights, high-quality profiles of both N₂O and CH₄ were obtained on ascent and descent, and no instrument damage resulting from the several flights.

Correlations of ALIAS-II N₂O and CH₄ measurements, and with O₃ measurements, are characteristic of mid-latitude air sampling, and as expected are markedly different in the tropics.

Vertical profiles of the tracer gas measurements have been used to calculate the time scales for entrainment of mid-latitude air into the tropics, a time scale found to be several months for the lower stratosphere.

ALIAS-II has been recently upgraded with more robust analog electronics and instrument fore-optics. Configured with two new tunable diode lasers, ALIAS-II is now flight-ready for participation in the Sage III Ozone Loss and Validation Experiment (SOLVE) mission, with a first deployment in Kiruna, Sweden, in October 1999. For SOLVE, the ALIAS instrument will dedicate its two-channels to measurements of N₂O and CH₄, with the additional capability for HCl measurements.

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Balloon-Borne *In Situ* CO₂ Measurements

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Research Objectives

The balloon-borne CO₂ instrument was included in the OMS payload in order to extend our results from the ER-2 instrument to higher altitudes. In particular, we sought to obtain profiles of the mean age of the air to >30 km at tropical and extratropical latitudes. Mean ages derived from tracer data provide insight into transport rates throughout the stratosphere and provide a convenient observation-based diagnostic for evaluating transport parameterizations in models used to assess the impact of stratospheric pollutants.

Previous measurements of CO₂ for low values of the N₂O tracer, at middle and high latitudes, were acquired in filaments originating at polar latitudes. These data had been interpreted as representing mean ages at altitudes above the flight levels of the ER-2. The balloon measurements were intended to check these inferences. Data for high altitudes in the tropics could not be inferred from filaments, and the goal for tropical flights was to define mean ages, age spectra, and vertical advection rates for the tropical stratosphere.

Summary of Progress and Results

The balloon-borne CO₂ instrument was flown four times in 1997 and once in 1998 during the Observations of the Middle Stratosphere (OMS) experiment. High-quality CO₂ data were obtained on all 5 flights. One of the most important results of the OMS flights was determination of typical mean age profiles for the tropics and midlatitudes. We found that mean ages in the extratropics were ~2 years older than tropical mean ages at the same altitude up to ~32 km, the maximum altitude of the balloon. This age difference represents a critical parameter for testing model simulations of stratospheric transport.

Tropical data were obtained in February and November 1997 from Juazeiro do Norte, CE, Brazil (7.1°S, 39.18°W). We obtained measurements of CO₂ up to 27 km in February 1997 and up to 32 km in November 1997. We had two flights separated by 9 days during the November deployment, and significant variability was observed in the profiles. Mean ages of ~3.75 years

were observed at 32 km in November 1997, and ages up to 4.5 years were observed in filaments of air from higher latitudes (as indicated by simultaneous observations of N₂O and the CFCs) at several altitudes during both of the November flights. Mean ages calculated from the February 1997 data are quite similar to those from November, but no obvious extratropical filaments were observed. We had also hoped to observe the propagation of the CO₂ seasonal cycle above ER-2 altitudes in the tropics. However, the seasonal cycle in the profiles above Juazeiro do Norte was not as clearly defined as in ER-2 profiles directly over the equator.

Extra-tropical data were obtained during the Photochemistry of Ozone Loss in the Arctic in Summer (POLARIS) experiment based in Fairbanks, Alaska (64.5°N, 147.5°W) on June 30, 1997, providing an excellent opportunity for direct comparison of our balloon-borne and ER-2 instruments. The instruments agreed to within their combined accuracy (0.1 ppm). At the maximum altitude of the balloon, the mean age of the air was 6.5 years, representing the oldest mean ages observed in the stratosphere to date. Unexpectedly, remnants of the 1996-1997 polar vortex were observed during this flight. Minimum SF₆ mixing ratios were observed in these vortex remnants, while the minimum CO₂ mixing ratios were observed at the maximum altitude of the profile, supporting the view that there may be a mesospheric sink for SF₆. Comparison of the relationships between CO₂ and other long-lived tracers (N₂O, CFC-12, CFC-11, and CH₄) in these vortex remnants with the background relationships reveals evidence that the mixing ratios in the remnants have been affected by a dispersive mixing process, resulting in a straightening of the CO₂:tracer relationships. This result could not have been obtained using aircraft data alone, since the aircraft only sampled air with low N₂O values in the vortex remnants, while the balloon encountered air with low N₂O both in the vortex remnants and aloft.

CO₂ and SF₆ data from our midlatitude flights from Fort Sumner, New Mexico (34.27°N, 104.16°W) on September 21, 1996 and May 18, 1998 reveal a region of nearly constant mixing ratio from 22 km and 25 km, respectively, to the maximum altitude of the balloon (~32 km). The corresponding mean ages in this region are 4.25-5.0 years. Similar regions of near constant CO₂ mixing ratio have been observed in data from balloon-borne flask samplers, suggesting that this is a persistent feature of the midlatitude stratosphere.

Mean ages derived from CO₂ agree with those derived from SF₆ to within ~10-20% for all of the OMS balloon flights, with the SF₆ ages consistently older. Possible reasons for the discrepancies are uncertainties in the SF₆ boundary condition, errors in the correction for nonlinearity in the growth rate of SF₆, or mesospheric loss of SF₆ propagating into the stratosphere.

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B. BALLOON-BORNE REMOTE MEASUREMENTS



Infrared Measurements of Atmospheric Constituents - Balloon Borne Measurements

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Research Objectives

Small lightweight infrared instruments were flown as piggyback payloads on larger balloon gondolas to obtain altitude profiles of compounds of interest to stratospheric chemistry, for validation of satellite observations. These flights were performed from Kiruna, Sweden as part of an ILAS (Infrared Limb Atmospheric Sounder, an ADEOS instrument) validation campaign in early 1997. Two flights were flown on the gondola of Camy-Peyret (CNES, France) and two on the Japanese gondola (Kondo, STE Laboratory). An additional validation flight was flown on Toon's (JPL) gondola from Fairbanks, Alaska in May 1997.

Our small, lightweight solar transmission instrument was flown as part of the Middle Atmosphere Nitrogen Trends Assessment (MANTRA) gondola (Strong, University of Toronto). Flight costs were provided by the Canadian Space Agency, and the flight was launched from Saskatoon in August 1998.

Summary of Progress and Results

Our infrared instrumentation includes several small liquid helium cooled atmospheric emission spectrometers. These instruments were designed to receive radiation from 20° above the horizon and measure the spectral emission in the 9μ - 13μ region as the balloon ascends. By studying the change in the spectral features with altitude, one can recover the change in the chemical compound causing the emission, and determine an altitude profile. A major balloon campaign was undertaken from Kiruna, Sweden during January, February, and March 1997. During this period a number of large balloon flights were performed. We flew on four of these flights. The flights on February 10 and 25 were on the CLD gondola of Kondo. Flights on February 26 and March 21 were on Camy-Peyret's LPMA gondola. HNO_3 altitude profiles were derived for all flights. These profiles were compared with the profiles obtained by the ILAS instrument on the ADEOS satellite.

The final piggyback flight with a small emission instrument was performed on May 8, 1997 from Fairbanks, Alaska. For this flight we incorporated our instrument into the JPL gondola of G. Toon. This flight was provided excellent data, with the stabilized gondola providing

improved signal to noise in our system. The data obtained during the flight has also been compared with ILAS data.

With NASA and NSF support, we also participated in a flight launched from Saskatoon, Saskatchewan on August 24, 1998 with flight costs provided by the Canadian Space Agency and Atmospheric Environment Service (Canada). We joined a number of Canadian colleagues in instrumenting a gondola using both old and new instruments to provide a long-term basis for mid latitude stratospheric nitrogen trends assessment. We used our high resolution (0.02 cm^{-1}) solar interferometer system, equipped with two detectors covering the spectral regions $700 - 1200\text{ cm}^{-1}$ (for HNO_3 , O_3 , N_2O , CH_4 , CFC-11 & CFC-12) and 2750 to 3200 cm^{-1} (for HCl). The flight went well and data were obtained with our instrument during sunset. Our data have been reduced to obtain profiles of several compounds which will be used with data from other instruments and will be incorporated into a MANTRA report.

Publications

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Far Infrared Measurements of Trace Gases

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Research Objectives

This program is the United States component of a NASA International Cooperative effort with Italian and British participation to study stratospheric ozone chemistry. Originally composed to provide balloon-based validation measurements for the Upper Atmosphere Research Satellite (UARS), the program was augmented with Methyl Bromide Global Coalition industry support to include measurements of stratospheric HBr for a better quantification of bromine-induced ozone loss. Additional objectives include the preparation of a database of far infrared stratospheric emission spectra, laboratory spectroscopic research to improve the line parameter database, and scientific collaboration in European aircraft-based measurements of ozone chemistry.

Summary of Progress and Results

A major regulatory issue for the protection of the Earth ozone layer is the quantification of ozone loss by bromine-containing source gases, principally the source gas methyl bromide used as an important soil fumigant. A key step for the justification of bromine regulation is the measurement of chemistry sink species, HBr, to verify bromine-induced ozone loss in the stratosphere. A program priority has been the analysis of a balloon-based measurement of the stratospheric concentration of HBr. This objective was completed in 1997 and the results have been incorporated in bromine chemistry revisions ([Chipperfield *et al.*, 1997] *Geophys. Res. Lett.*, 24, 3025-3028] and in recent assessments of the ozone depletion potential of methyl

bromide ([Ko *et al.*, 1998] *J. Geophys. Res.*, 103, D21, 28187-28195). The final balloon flight provided limb scan emission spectra of the stratosphere of uniquely high spectral resolution and sensitivity. This data has been assembled into a hardcopy atlas and is being formatted into a web-accessible database. The atmospheric spectral data provided frequency measurements which, in combination with cooperative laboratory research by the European Laboratory for Non-linear Spectroscopy (LENS), resulted in improvements to basic spectroscopic line parameters [De Natale *et al.*, 1997]. Additional laboratory research has been conducted in a long-standing collaboration between NASA LaRC, the National Institute of Standards and Technology (NIST), and the University of Oregon. This work exploits the Tunable Far IR technique developed by the National Institute for Standards and Technology for precision measurements of linewidth parameters which are required to retrieve accurate stratospheric trace gas concentrations from emission spectra. Finally scientific participation continues in the European-based Spectroscopy of the Atmosphere using Far IR Emission program for the study of polar ozone chemistry.

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Far IR Radiometer for OH

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Research Objectives

We have two stratospheric hydroxyl radical (OH) radiometers, which are used for balloon observations in the far infrared region of the spectrum. The older instrument (FILOS) uses three Fabry-Perot resonators to resolve stratospheric limb emission of OH at 101 cm^{-1} ($99\text{ }\mu\text{m}$) and 118 cm^{-1} ($85\text{ }\mu\text{m}$). The spectral resolution of 0.002 cm^{-1} is used to match the width of the stratospheric OH emission. The instrument is compact and designed to fly jointly with other balloon measurements. The goal of this instrument is to determine OH concentrations from 35-45 km with better than 10% accuracy. An equally compact heterodyne balloon OH instrument (BOH) has been developed as a breadboard for the Earth Observing System-Microwave Limb Sounder (EOS-MLS) 2.5 THz receiver. Under an agreement the EOS-MLS project, this breadboard can also be used for balloon measurements of OH in the stratosphere. However, all costs unique to the balloon measurements have to come from the Upper Atmospheric Research Program. This new instrument should have 20 times better sensitivity for OH in the 20-30 km altitude range, where OH chemistry competes as the dominant ozone loss mechanism. This new instrument will also have some capability for measurements of water and ozone. The OH concentrations in both instruments are measured as a function of the diurnal cycle and can be used to validate odd hydrogen chemistry in conjunction with other measurements.

Summary of Progress and Results

The Far Infrared Limb Observing Spectrometer (FILOS) measures chemical species in the upper atmosphere using limb emission in the far infrared region of the spectrum. The FILOS balloon instrument made its first scientific flight on May 15, 1989, detecting OH, O₃, HDO, and water at 101 cm^{-1} . This flight culminated an extensive laboratory development program that has resulted in a very well characterized system [Pickett and Peterson, 1993]. Our measurements agree with a photochemical model to within 5% [Pickett and Peterson, 1996].

The balloon instrument currently is tuned to two 0.054 cm^{-1} bands near 101.3 cm^{-1} ($99\text{-}\mu\text{m}$ wavelength), and 118.2 cm^{-1} ($84\text{-}\mu\text{m}$ wavelength). Each band uses a combination of two fixed Fabry-Perot etalons at 4 K for order filtering and uses a common scanning Fabry-Perot etalon at ambient temperature. The instrument parameters are such that FILOS can be accommodated on

the service floor of the JPL gondolas, allowing joint flights with larger instruments. Table 1 lists the FILOS instrument balloon flights for the last decade.

Table 1. Recent FILOS Flights

Date	Latitude ($^{\circ}$ N)	Longitude ($^{\circ}$ W)	Balloon Height (mbar)
Feb. 20, 1992	36.8-37.1	251.5-258.0	2.9-3.3
Sept. 29, 1992	34.6-35.8	256.8-259.8	3.7-5.1
May 31, 1993	34.4-34.9	253.2-255.7	3.8-10.
Sept. 25, 1993	32.3-34.5	256.9-259.9	4.0-4.9
May 15, 1994	34.8-35.8	254.8-255.8	4.1-6.2
May 24, 1998	34.5	255.8	4.6

A balloon-based prototype heterodyne 2.5 THz radiometer had its first flight on May 24, 1998 from Ft. Sumner, New Mexico. The purposes of this balloon instrument are to:

- Provide early real-world use of selected components that will be used on the flight instruments;
- Obtain early views of stratospheric OH using the frequencies and techniques that will be used in flight; and
- Gain operational experience with a balloon instrument that can be used for sub-orbital validation after launch.

The balloon instrument included a JPL waveguide mixer, a prototype laser LO, and a brassboard filter bank. A block diagram of this BOH instrument is shown in Figure 1. The overall instrument size is identical to FILOS, namely 60 cm \times 120 cm \times 48 cm. The telescope primary is also identical to FILOS. It is 10 cm in diameter and has a 65-cm focal length. The methanol laser operates at 2522.782 GHz and three second-IF frequencies are selectable. Currently these are located so that the filter bank is centered on OH lines at 2509.949 and 2514.317 GHz or on a water line at 2531.917 GHz. The diplexer is a 4-port Martin-Puplet interferometer that is used to combine the thermal emission from the sky with the laser local oscillator.

The mixer, laser LO, and the filter bank worked well during the flight, but a coolant pump failed causing the thermal control to be much worse than desired. Fortunately, for a 40-min period midway through the flight, the thermal drift was small enough to lock the laser and take data. The fitted profile of OH is similar to values previously obtained from FILOS in May at Ft. Sumner, but the uncertainty is >10 ppt due to the thermal drifts.

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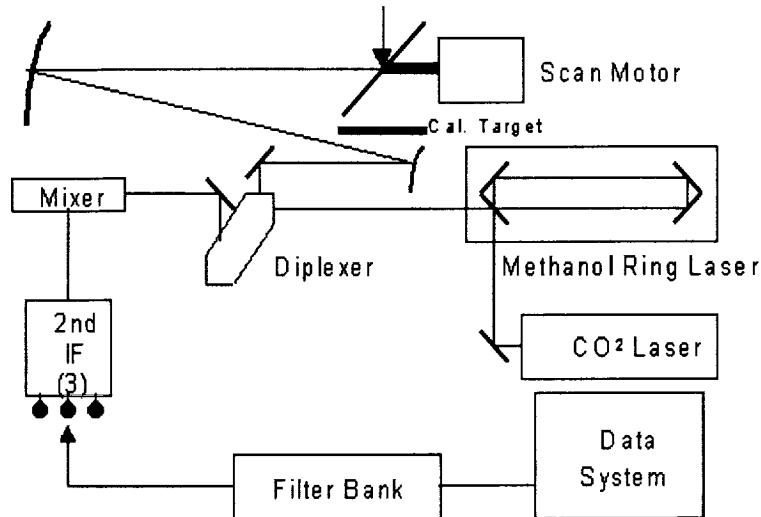


Figure 1. BOH block diagram.

Publications

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Multisensor Measurements

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Research Objectives

The Multisensor Measurements Task provides for continuing technical, logistical, and operational support for stratospheric balloon flights to measure the abundance and altitude distribution of key chemical constituents in the upper atmosphere. Several gondola systems are used which carry single- and multi-instrument payloads consisting of *in situ* and remote sensing instruments from JPL and other institutions in the United States and abroad. Data are obtained on the altitude profiles for a number of chemically-coupled species from one or more simultaneous flights in the same airmass which are used for instrument intercomparison purposes and for validation of atmospheric chemical models.

Summary of Progress and Results

The first full-up science flight of the multi-sensor (OMS) gondola was flown on September 21, 1996 from Fort Sumner, New Mexico. The Toon Mark IV was flown successfully one week later on September 28 from the same location.

While plans called for shipping the OMS gondola and payload to Brazil later in the fall of 1996, several inordinate delays were encountered in obtaining permission from the Brazilian government to fly in their country. Ultimately, the shipments and flight personnel did not arrive in Brazil until January 1997, and a successful flight was finally mounted from Juazeiro Do Norte on February 14.

After the flight in Brazil, preparations began in earnest for an extended flight campaign from Fairbanks, Alaska. Overall, four successful flights were made during this campaign; these included the SAO payload on April 30, the Mark IV on May 8, the OMS on June 30, and the Mark IV a second time on July 8.

During the latter part of October 1997 the OMS gondola and support equipment were again shipped to Edwards Air Force Base for subsequent shipment to Brazil. The balloon flight support personnel, science teams, and gondola systems all arrived in Juazeiro Do Norte in early November and were able to mount a first flight on November 11. The landing on this flight was nominal with minimal damage to the gondola and the flight personnel were able to recover and refurbish the gondola in time for a second flight on November 20. Some noise problems were

experienced during these two flights (subsequently determined to be an NSBF problem) but both flights returned useful data from all the instruments on board.

In May, the OMS gondola and payload and the SLS gondola with Herb Pickett's FILOS and BOH instruments on board were shipped to Fort Sumner in preparation for one flight of each system. The OMS gondola was launched first during these operations on May 18, and the Pickett payload was flown on May 24. Good data was obtained from both of these flights, but during the landing of the latter the SLS gondola suffered severe damage and minor damage was inflicted on the instruments.

This was followed by an extended period without any flight operations during which the balloon flight support personnel refurbished and upgraded the balloon flight systems and assisted the instrument flight teams in doing the same. Preparations began in the early fall of 1999 for extended balloon flight operations from Kiruna, Sweden during the period from November 1999 to February 2000. In the interim, one more successful flight was made from Fort Sumner in October with the Pickett FILOS-BOH payload.

At the time of this writing, the balloon flight systems and personnel have been deployed to Wright-Patterson AFB in Ohio for subsequent shipment to Kiruna.

Publications

None

Millimeter and Submillimeterwave Radiometry

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Research Objectives

The objective of this program is measure abundance and variability of stratospheric trace constituents that influence stratospheric ozone using balloon and aircraft-borne millimeter and sub-millimeter wave spectrometers. The present instrumentation uses 3 submillimeterwave mixers at 637 GHz, 604 GHz, and 311 GHz to simultaneously measure the abundance of O₃ and ClO, a key indicator of Cl-catalyzed O₃ destruction, HCl, HO₂, HNO₃, N₂O and H₂O in the stratosphere and upper troposphere. This program also provides a background for development of satellite instrumentation that can yield measurements on a global scale. Technology developed by this program has been used in the Microwave Limb Sounder (MLS) instrument on Upper Atmosphere Research Satellite (UARS) and will be essential to the development of the proposed MLS instrument on the Earth Observing System (EOS) platform.

Summary of Progress and Results

During the past three years, the balloon and aircraft versions of the submillimeter wave limb sounder (SLS) have been part of three field experiments. In April 1997, the balloon SLS was part of a balloon payload flown from Fairbanks, Alaska to validate measurements of instrumentation onboard the ADEOS satellite and to examine the chemical composition of the high latitude summer stratosphere. The aircraft version of the SLS was flown as a component of the NASA ER-2 payload during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission. This mission was also based at Fairbanks, Alaska during May through September 1997. In POLARIS, the SLS instrument was flown on four transits between Fairbanks and Moffett Field, California to survey the latitudinal and seasonal variation of the abundance of O₃, HNO₃, N₂O and H₂O. SLS was also flown as part of the TEFLUN (TRMM satellite validation underflights) ER-2 payload in May 1998 from northwest Florida. In TEFLUN, SLS measured the abundance of H₂O and O₃ above convective weather systems.

Three papers from the analyses of SLS observations from balloon in the Arctic winter during the Second European Stratospheric and Mid-latitude Experiment were published (or submitted) [Stachnik *et. al.*, 1999; Engel *et. al.*, 1997, 1999]. These papers examine details of the heterogeneous conversion process of chlorine reservoir species to active form during the polar winter. Results of two earlier mid-latitude balloon flights were published [Osterman *et al.*, 1997;

Jucks *et al.*, 1996]. These reports compare model calculations to the measured abundance profiles of several key stratospheric species involved in gas phase ozone loss processes.

The effect of high altitude clouds (cirrus) has been identified as a possible concern in the EOS Microwave Limb Sounder (MLS) retrieval of water vapor in the upper troposphere. Although significant theoretical work has been done on this problem, (e.g., [Stackhouse and Stephens, 1991] (*J. Atmos. Sci.*, 48, 18); [Evans and Stephens, 1995] (*J. Atmos. Sci.*, 52); [Czekala, 1998]; (*Geophys. Res. Lett.*, 25, 10)) relatively little directly applicable experimental data is available. The SLS aircraft instrument covers key spectral bands near 640 GHz, similar to EOS MLS, and a water emission line at 325 GHz. SLS may be able to provide basic data useful to the EOS MLS effort on the radiative properties of cirrus using a similar viewing geometry and measurement frequencies. Radiative transfer calculations of the correlation between 600 GHz and 300 GHz radiance from the upper troposphere have been compared to SLS observation in these bands made during the POLARIS and TEFLUN aircraft flights. An improved optical layout including two polarization split 600 GHz receivers, and one 325 GHz receiver has been developed. The design uses a rotary chopper to provide signal-reference samples at 20 Hz to minimize the thermal drift. The switching scheme has been bench tested using the 325 GHz (H_2O) receiver and a lock-in signal processor as the demodulator. The required radiometric sensitivity of less than 1 K for 1 GHz pre-detection bandwidth for a 1-second integration period was demonstrated.

Publications

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Stratospheric Fourier Spectrometry

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Research Objectives

This investigation measures the atmospheric abundances of a wide variety of gases which influence atmospheric chemistry or are tracers of transport. These measurements are made by the JPL MkIV Interferometer, a high resolution FTIR (Fourier Transform Infra-Red) spectrometer which operates in the solar absorption mode from the ground, balloons, or aircraft. The high resolution (0.01 cm^{-1}) and broad spectral coverage (650 to 5650 cm^{-1}) of the MkIV instrument allow it to measure over 30 different gases simultaneously in the same airmass including CO_2 , HCN , CH_4 , N_2O , OCS , CHClF_2 , CCl_2F_2 , CCl_3F , CCl_4 , $\text{CCl}_2\text{FCFCl}_2$, O_3 , NO , NO_2 , HNO_3 , HNO_4 , N_2O_5 , ClNO_3 , HOCl , HCl , HF , COF_2 , CF_4 , SF_6 , H_2O_2 , HCOOH , H_2CO , CO , C_2H_2 , C_2H_6 , HCN , H_2O , plus numerous isotopic variants. These observations are used to evaluate trends, to ground-truth satellite observations, and to test model predictions over a range of conditions (latitudes, seasons, altitudes, aerosol loading).

Summary of Progress and Results

Four balloon flights were undertaken during the period 1996-1997: from Lynn Lake, Manitoba, in July 1996; from Ft. Sumner, New Mexico, in September 1996; and from Fairbanks, Alaska, in May and July 1997. Papers submitted or published which used these MkIV balloon data covered such diverse areas of scientific interest as the chlorine budget [Sen *et al.*, 1999], the response of chlorine partitioning to the Pinatubo eruption [Webster *et al.*, 1999; Jucks *et al.*, 1999], nitrogen partitioning [Osterman *et al.*, 1999], mixing and denitrification [Rex *et al.*, 1999], stratospheric water vapor [Johnson *et al.*, 1999], intercomparison of MkIV balloon and ER-2 aircraft observations [Toon *et al.*, 1999a], and intercomparison of MkIV balloon and ILAS observations [Koike *et al.*, 1999].

In addition to these balloon flights, over 200 days of ground-based observations were performed in support of the Network for Detection of Stratospheric Change (NDSC). These column measurements were made from various sites in 1996 including JPL, Lynn Lake, Manitoba, Ft. Sumner, New Mexico, and JPL's Table Mountain Facility (TMF). These TMF observations were part of a FTIR intercomparison [Goldman *et al.*, 1999] in which four FTIR spectrometers

took ground-based observations simultaneously and then compared results. Additionally, 47 days of observation were performed from Fairbanks, Alaska, from March to September 1997 [Toon *et al.*, 1999b; Lloyd *et al.*, 1999] as part of POLARIS. More recently 44 days of observation were performed from the Barcroft Laboratory (3.80 km altitude), in the White Mountains of California, over the period October 1998 to July 1999. The MkIV instrument was controlled remotely from JPL over a cellular phone and powered by batteries recharged by solar panels. Barcroft is a much less polluted site than JPL or TMF, being more than 350 km from the nearest large city, and being above the boundary layer.

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Measurement of HO₂ and Other Trace Species in the Stratosphere Using a High-Resolution Far-Infrared Spectrometer

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Research Objectives

Our first scientific objective is to improve the state of understanding of chemistry and transport in the middle and upper stratosphere, by making simultaneous measurements of the abundances of over 25 species and isotopes, and interpreting these in terms of current chemical models and transportation processes. Our second objective is to validate satellite measurements by observing the same air mass at the same time as the satellite; we have provided this important service for both the Upper Atmosphere Research Satellite (UARS) and the Advanced Earth Observing Satellite (ADEOS). These two objectives are frequently pursued in parallel.

Summary of Progress and Results

Observations are made continuously, day and night, with a remote-sensing Fourier-transform spectrometer (FIRS-2), from a balloon platform, in the far-infrared and mid-infrared spectral regions simultaneously. Our research is based on data from 10 flights of the FIRS-2 in the period 1987-1997, all of which were successful. These flights covered a range of latitudes, seasons, and volcanic conditions; this time series of observations, under a variety of conditions, is crucially important in helping us to reach many of our most significant conclusions.

A particular highlight of the FIRS-2 is that it is the only instrument that can individually measure concentration profiles with high precision for all key reactive molecules involved in the photochemical destruction of stratospheric ozone, all reservoir compounds for ozone-destroying radicals, and most of the upper-tropospheric source gases.

Our measurements of OH and HO₂ in the middle stratosphere yield a ratio of these species which is roughly 10 times better than the uncertainty in this ratio from chemical reaction rate modeling, so our data provide a stringent test for any model. On this basis we have suggested changes in the reaction rate constants which would produce better agreement with our field observations. Using the same data, we have compared our results with those of researchers using satellite

measurements of OH and have reached significantly different conclusions than they have regarding the likely values of these same reaction rate constants; we are collaborating with these researchers to find a solution to this issue. A particular result of our work is that there is as yet no resolution to the long-standing "ozone deficit problem" above 45 km.

We have measured nitric acid (HNO_3) in the lower and middle stratosphere during times of very small (background) as well as very large (Pinatubo) aerosol densities. We have compared our results with those of models, and find that the models significantly overestimate HNO_3 in the middle stratosphere, especially at background levels and in the middle stratosphere. This disagreement can be reduced by changing some reaction rate constants, but strong differences still remain, suggesting that yet-unknown paths still exist for the loss of HNO_3 , possibly increased photolysis near 200 nm wavelength.

Both our measurements and those of another group show that hydrogen peroxide (H_2O_2) is present in the stratosphere in amounts which are consistently much lower than predicted by standard chemical modeling, suggesting that there is an unknown sink for this species. We have considered many potential mechanisms to explain this effect, but have not yet found a explanation which is also consistent with available kinetic data and the observed altitude profiles of other species.

By way of contrast with the case of HNO_3 , our measurements of the hydrochloric acid (HCl) as a fraction of total chlorine, under the same wide range of aerosol conditions, shows general agreement with standard photochemistry, with no significant differences.

We have measured the mean age of air in the stratosphere, i.e., the time since it crossed the tropopause boundary, by combining global measurements from two UARS instruments with calibrations from two balloon-borne instruments (including FIRS-2), and analyzing the resulting 13-year record for the annual cycle of water vapor (H_2O) injected into the stratosphere in the equatorial region, as this cycle slowly propagates upward over a period of several years. We see evidence that the year to year variation in strength of the annual water cycle is influenced from below by the tropical sea surface temperature, and from above by the quasi-biennial oscillation of the stratosphere.

We have also improved the spectroscopic parameters for many important molecules in the far infrared region. In collaboration with colleagues at the University of Paris, we have incorporated the ability to calculate line mixing for Q-branches of CO_2 and N_2O in our radiative transfer algorithm. Q-branches for both of these bands overlap with the spectral features we use to retrieve ClNO_3 and N_2O_5 and the line mixing must be calculated for accurate retrievals. We have also improved important spectroscopic parameters for H_2O , N_2O , ClNO_3 , HO_2 , OH , H_2O_2 , N_2O_5 , and acetone. Many of these spectroscopic updates are now, or in the future will be, incorporated into the HITRAN spectroscopic database of which two members of the group belong to the science team.

We have made several advances in instrumentation during this period. A key advance is that we have worked to develop a new type of beamsplitter for the FIRS-2 which can be used over the very wide range of wavelengths from about 8 to 130 micron; this beamsplitter was used on our most recent flight, and provides significantly improved accuracies of measurement of many species, as well as opening up the 8-15 micron range and allowing us to measure additional species. A second advance is that we have built an on-board data recorder which will free us

from the potential of unwanted radio interference in our data telemetry stream for future flights. A third advance is that we are developing a design for a lightweight spectrometer (FIRS-3) which could be flown on small balloons, long duration balloons, and remotely-piloted aircraft, thereby increasing our potential range of launch sites to include the tropics and polar regions.

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C. GROUND-BASED MEASUREMENTS



Latitudinal Tropospheric Concentration Distributions of Selected Halocarbons and Hydrocarbons**Principal Investigator:** Donald R. Blake**Co-Principal Investigator:** F. Sherwood Rowland**Organization:** Department of Chemistry
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World-wide assay of the atmospheric burdens of halocarbons, hydrocarbons, alkyl nitrates, and carbon monoxide were carried out on tropospheric air samples collected in remote locations over two week periods every three months, covering the latitudinal range from 71°N to 47°S. The air samples (approximately 80/collection period) were analyzed in our laboratory for about 50 compounds. The latitudinal distribution measurements for CCl_4 , CCl_3F , CCl_2F_2 , CH_3CCl_3 , and CH_4 form part of a continuing set of data from January 1978. Correlations between methyl bromide and other biogenically and anthropogenically emitted gases provide information to differentiate between sources and estimate their strengths and latitudinal distributions. The latitudinal distribution of relatively short lived gases such as nonmethane hydrocarbons (NMHCs), alkyl nitrates, and alkyl halides, provides information regarding source distribution, emission strengths, and lifetimes. Although these gases are short lived they can play a role in boundary layer chemistry and in some circumstances can also affect stratospheric chemistry.

Summary of Progress and Results

Eleven latitudinal sample collections have been completed since the start of this grant in January 1997. Latitudinal profiles for the long-lived gases CFC-11, CFC-12, CFC-113, methyl chloroform, and carbon tetrachloride all indicate that their atmospheric emissions are continuing to decrease. World average mixing ratios of these five gases in parts per trillion by volume for April 1997, April 1998, and April 1999 are given below:

Year	CFC-11	CFC-12	CFC-113	MeCCl_3	CCl_4
1997	263.88	525.22	83.19	86.89	109.73
1998	262.31	528.04	82.88	75.44	108.21
1999	260.19	532.19	82.19	59.32	106.19

The rate of increase in CFC-12 has slowed in recent years but its concentration continues to increase. Methane's world average concentration on the other hand is starting to rise again. During the mid-90s the rate of increase slowed to 2-3 ppbv/year but since 1997 the rate has

increased to 5-6 ppbv/year. It has been reported that reductions in natural gas leakage in the former Soviet Union was contributing to the decreasing trend of methane's increase.

Methyl bromide concentrations obtained from this latitudinal study were originally solely used in making the observation that methyl bromide exhibited a seasonal behavior in the Northern Hemisphere. The paper discusses the importance of the seasonality, and we estimate that when seasonality is taken into account, about 10% less Northern Hemisphere (likely anthropogenic) emissions are needed to explain the N/S ratio. Yung *et al.* from JPL are working on a methyl bromide paper that compares their model results with our observed concentrations.

Data for methane mixing ratios observed in 3955 ground level whole air samples collected between 1980-1997 have been compiled and partitioned into latitudinal bands used to calculate "world averages." A relatively steady increase in methane concentration at all latitudinal regions between August 1980 and September 1997 has been observed. The rate of increase was faster in the 80s and has slowed to 3 pptv/year during the last two years. Because of the lower photochemical removal rate by hydroxyl during the winter, higher mixing ratios were observed in September and December in the Northern Hemisphere, while the opposite is true for the Southern Hemisphere. Therefore, the N/S gradient is larger during September and December. A very pronounced "ridge" (more gradual N/S gradient) was observed around 1982, and less so in 1989, 1991, and 1993. In contrast, the relative methane concentration levels in the Southern Hemisphere were markedly lower between 1983-1988. Two additional depressions occurred between 1989-1990 and 1994. The March and June 1997 data suggests a pronounced ridge for 1997. The smaller N/S gradient suggests a mechanism of more rapid inter-hemispheric transport where the concentration levels in the northern hemisphere are diluted by the cleaner Southern Hemispheric air, accompanied by a corresponding increase in Southern Hemispheric concentrations.

These ridges correspond to the magnitude and occurrence of El Niño events. El Niño events are marked by a decrease in the strength of east to west equatorial trade winds and the spread of warmer than normal equatorial Pacific sea surface temperature. The higher sea surface temperatures over the eastern Pacific rim produce more typhoons and brings rain and floods to the U.S. west coast and Chile. The September 1997 presence of typhoon/tropical storm Nora in normally very dry California is a good example of effects from El Niño. These methane data strongly suggest that the inter-hemispheric transport is strengthened during El Niño years.

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Infrared Fourier Transform Spectroscopy in Support of the Network for the Detection of Stratospheric Change (NDSC)

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Research Objectives

The objectives of this work are to use infrared spectroscopy to study the chemical and physical processes which control ozone in the stratosphere and upper troposphere. Using high resolution Fourier transform spectrometers, based on the ground and on aircraft, we obtain column amounts for ozone and a number of trace gases important to its chemistry, including NO, NO₂, HNO₃, HCl, HF, ClONO₂, as well as water and several tracers of atmospheric motions.

Summary of Progress and Results

As part of one of the primary observing sites of the NDSC we have installed a Bruker model 120M Fourier transform spectrometer at Thule, Greenland (Lat.: 76N, Long.: 69W). This instrument will be operated remotely from our laboratory in Boulder to make observations of infrared spectra for those periods when the sun is visible from Thule. Observations have been made for the autumn period of 1999. In preparation of these measurements, and to insure that observations made throughout the NDSC could be intercompared with validity, we have participated in a number of intercomparisons and evaluations conducted for infrared spectrometers of the NDSC. To assist in validation and calibration of the various infrared spectrometers in the network we have developed a sealed cell with fused sapphire windows containing a low pressure of HBr. This gas, which is a negligibly small component of the natural atmosphere, has well known, narrow spectral lines in a transparent atmospheric region, which makes it an excellent absorber for interferometer calibration. While investigating the HBr cells, for use as high-resolution standards, we discovered the need to consider the hyperfine structure in its spectrum, which resulted in one of the publications listed below. We have been active participants in defining the procedures and protocols for intercomparison and validation of the infrared instruments of the NDSC and for the observations of geophysical parameters they will produce.

Publications

Coffey, M. T., A. Goldman, J. W. Hannigan, W. G. Mankin, W. G. Schoenfeld, C. P. Rinsland, C. Bernardo, and D. W. T. Griffith, Improved vibration-rotation (0-1) HBr line parameters for validating high resolution infrared atmospheric spectra measurements, *J. Quant. Spectrosc. Radiat. Trans.*, 60, 863-867, 1998.

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Stratospheric and Mesospheric Trace Gas Studies Using Ground-Based Millimeter Wave Receivers

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Research Objectives

Over the three-year period, 1997-1999, the objectives of this research have been: (a) to carry out both field measurements of polar stratospheric ClO at extremes of the Arctic and Antarctic, and intercomparisons between our standard ClO measurement spectrometer and dedicated NDSC (Network for Detection of Stratospheric Change) instruments or correlative instruments that have recently been installed at Ny Ålesund (on the Arctic island of Spitzbergen) and McMurdo Base (Antarctica), in preparation for turning over routine measurements to these instruments; (b) to improve the sensitivity and extend the frequency coverage of an older mm-wave spectrometer for new field work; (c) to finish the analysis of a body of data collected during 1993 and 1995 at the South Pole for the trace gases O₃, N₂O, NO₂, and HNO₃, and to begin the collection of a new annual cycle of data at the South Pole using the improved instrument mentioned above in (b).

Summary of Progress and Results

Our most sensitive chlorine-monoxide (ClO) measuring spectrometer was shipped late in 1996 to the Ny Ålesund research station on the island of Spitzbergen (an NDSC station at 78.9 N, 12 E) for ClO measurements and participation in an intercomparison campaign in the spring of 1997, with cooperation and partial support for logistics from the Environment and Climate Program of the European Union. Our instrument was compared with three others from the University of Bremen, the University of Karlsruhe, and the Communications Research Laboratory, (Japan). We were at Ny Ålesund with our instrument for about 6 weeks in total, and despite poor observing conditions, a reasonably successful intercomparison campaign was achieved. Results have been written up and submitted for publication.

In the austral springs of 1997 and 1998 (late August to early October) we returned to McMurdo Station, Antarctica for intercomparison measurements with an NDSC ClO-measuring mm-wave spectrometer installed in 1996 at nearby Scott Base, about 1/2 mile from our instrument location. The goal of this is to provide calibrated continuity of the record begun by us at McMurdo in 1986-1987 with the monitoring now being done on a quasi-continuous basis by the NDSC spectrometer. Two years were planned to allow for adequate data under poor conditions, equipment problems, or other hazards of data-gathering in a remote and sometimes difficult

environment. All data has been independently analyzed from the two intercomparison years, and a detailed comparison of results is about to be undertaken.

A planned upgrade of our older mm-wave receiver/spectrometer to replace a Schottky detector with a significantly more sensitive superconducting tunnel-junction (SIS) detector has been delayed. We have however finished a planned increase of its frequency coverage by installing a second local oscillator for quick frequency switching over the entire range from ~230 to 280 Ghz. A very high performance SIS mixer was obtained, but integration and testing of this in a complete receiver system was stymied through continued delays by various suppliers in the promised production of a relatively compact, reliable, and efficient closed-cycle 4 Kelvin refrigerator suitable for remote-station field use. By the time we were finally able to get delivery of the desired type of refrigerator from Sumatomo, Inc. (January 1998), insufficient time was left in which to complete the rebuilding and field debugging needed to insure totally reliable operation. To meet an immovable deadline for shipping the equipment to the South Pole, we therefore refitted the system with the original Schottky receiver to avoid losing at least one year before another opportunity would come to install the experiment at the Pole. The instrument was shipped on time, and installed at the Pole to carry out an annual cycle of measurements. The expanded frequency span is available, and the Schottky mixer was found to be functional over the desired range from 230 GHz (CO) to 278 GHz (NO_2), although without the much higher sensitivity that an SIS device would have provided. Observations have been in progress since February 1999 (see below). Overall sensitivity is similar to that used in previous successful work with this instrument at the Pole.

Our second mm-wave spectrometer (see above) was moved to the Amundsen-Scott South Pole Station (90.0 S) in January 1999. About 2 weeks were spent at the Pole uncrating, installing, and testing the equipment, before turning it over to a winter-over technician for day-to-day observations. The goal of these observations is to complete another quasi-annual cycle of measurements on O_3 , HNO_3 , N_2O and NO_2 for comparison with those completed in 1993 and 1995, and to add observations of the relatively inert stratospheric-mesospheric tracer CO. The latter should allow us to better characterize high-altitude transport over the pole. Three nearly-complete annual cycles under conditions of relatively heavy sulfate aerosol loading (1993, from Mt. Pinatubo), diminished sulfate and other volcanic aerosol loading (1995) and the present very low background levels of aerosol, should provide a reasonably comprehensive behavioral climatology for these measured species over the range ~16-45 km (and up to 60-70 km for CO). Particular emphasis is being given to the behavior of NHO_3 as a key to NO_y , and to new observations of CO. Measurements are being made 6 days per week, weather and equipment permitting, on a cyclic basis with one to two observations per week for each of several species (seasonally varying). By mid-August 1999, over 3400 spectra had been taken, with the annual cycle about half completed.

Publications

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Support for NASA-Sponsored Research Projects, Including the Network for the Detection of Stratospheric Change, at Mauna Loa and American Samoa

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Research Objectives

The Climate Monitoring and Diagnostics Laboratory (CMDL) operates four Baseline Observatories at Barrow, Alaska; Mauna Loa, Hawaii (MLO); American Samoa (SMO); and at the South Pole. At two of these, MLO and SMO, CMDL supports NASA Upper Atmosphere Research Program (UARP) and/or Atmospheric Chemistry Modeling and Analysis Program (ACMAP) Projects. This support includes housing, operating, and maintaining NDSC equipment for external PIs, supplying electricity and liquid nitrogen, providing data collection and transfer infrastructure, and being responsible for shipping and transport of equipment, supplies, and personnel.

Summary of Progress and Results

A listing of the UARP and ACMAP sponsored projects operated and supported by NOAA/CMDL at MLO and SMO are presented below:

MLO

NDSC Microwave Water Vapor Instrument

Principal Investigator

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Ultra-High Resolution FTIR

F. Murcray
University of Denver

NDSC Ozone Lidar

S. McDermid
NASA/Jet Propulsion Laboratory

NDSC Mobile Ozone Lidar

T. McGee
NASA/Jet Propulsion Laboratory

NDSC Microwave Ozone Sounder

A. Parrish
University of Massachusetts

SMO

Principal Investigator

AGAGE Gas Chromatograph

R. Weiss

Scripps Institution of Oceanography

MLO Facility: The highlight of this reporting period is the completion and occupation of the newly constructed NDSC building at the MLO site, 11,140 ft above sea level on Mauna Loa mountain constructed by NOAA as its contribution to the NDSC network. This 3500 ft² state of the art building is straddled by an 800 ft² solar observing deck with essentially unobstructed horizon-to-horizon views. Interior mounted solar and lidar instruments view the firmament through instrument chimneys, some capped by motorized doors. The move of NDSC instrumentation to the new building was accomplished with minimal downtime ranging from a few hours for the NIWA/CMDL NO₂ UV-Vis spectrometer to two weeks for the NOAA aerosol and temperature lidar.

The NDSC building affords about 3 times the research space of the prior structures formerly housing the NDSC instrumentation. The MLO staff has installed a comprehensive fiber optic network, internet hub and server system in the NDSC Building which allows data from all of the MLO NDSC programs to be transmitted in real time to off-site PIs. This includes huge amounts of NASA/JPL lidar data, NRL microwave radiometer derived water vapor mixing ratios, University of Massachusetts stratospheric microwave ozone profiles, and solar spectra from the University of Denver FTIR.

In the coming year, redundancy will be built into the UPS and data server systems with the view of attaining near 100% operational time of the fiber optic/Internet data system. Lightning at the MLO site is the main cause of data transmission disruptions. In addition, automatic alarms will be built into the power/data stream system to alert the computer systems manager to potential problems through a telephone/pager link. It is the goal of the MLO staff to reduce downtime from data transmission interruptions to a few data hours per program year.

SMO Facility: The NASA funded AGAGE gas chromatograph and support equipment has been moved to a newly constructed, air conditioned, hurricane proof cinder block building constructed by NOAA specifically for GC measurements. In September 1999, a new telephone company providing cellular telephone service on the island ran a fiber optic line to a new relay tower at the SMO facility. Discussions are underway with this company to see if it will be possible to transmit the AGAGE GC data in real time back to Scripps. At present this data goes over expensive and unreliable telephone lines at very slow rate, if at all.

Publications

None

NDSC Ozone Lidar and Instrument Support

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Research Objectives

In earlier stages of this program the JPL Atmospheric Lidar Team has developed and established laser remote sensing laboratories at the Table Mountain Facility (TMF, 34.4°N) in Wrightwood, California, and at the Mauna Loa Observatory (MLO, 19.5°N), Hawaii. Both of these sites are stations within the international Network for the Detection of Stratospheric Change (NDSC). The primary and long-term goal is to make regular measurements, at least 2-3 times per week on average at each site, of the atmospheric profiles of ozone, temperature and aerosols to aid in the detection of changes in the ozone profile and to provide information to assist in the understanding of the reasons for such changes. The results from the TMF and MLO lidars are archived in the NDSC database to add to the global perspective of atmospheric change attained by the network. In the short-term, the results from the ground-based lidars provide correlative and ground-truth measurements for instruments onboard Earth orbiting satellites and the Space Shuttle, e.g., the Upper Atmosphere Research Satellite (UARS), and onboard research aircraft such as NASA's ER-2 and DC-8. Also in the short-term, we can observe and study the day-to-day and seasonal variability of these atmospheric parameters.

Summary of Progress and Results

The stratospheric lidars at TMF and MLO are each averaging more than 100 measurements per year for each of the parameters measured, i.e., ozone, temperature, and aerosol profiles. The TMF lidar has been operational since February 1988 and the newer lidar was moved to MLO in the summer of 1993 where it commenced routine measurements shortly thereafter. The following paragraphs identify some of the significant achievements over the last three years.

Lidar aerosol and ozone measurements at TMF were combined with microwave ozone measurements to try to quantify the effects of the Pinatubo eruption on the ozone concentration profile [Parrish *et al.*, 1998]. The results show a clear correlation between the aerosol density and reduced ozone values.

Together with the RIVM lidar group in The Netherlands we made the first observation of the signature of OH fluorescence in the 308 nm lidar returns at Lauder, New Zealand, and TMF [Brinksma *et al.*, 1998]. The fluorescence signal was seen as a layer, several kilometers thick, at altitudes above 80 km. Using the unique tuning capabilities of the JPL stratospheric lidars it was possible to tune the laser on and off OH resonance, using a laboratory OH source for a reference,

and thus confirm that the atmospheric signal was indeed due to OH. We were also able to estimate the OH ground-state concentration at these altitudes.

Significant progress has been made on an analysis and intercomparison of the methods and algorithms for the derivation of temperature profiles used by different groups within the NDSC. The algorithms used by JPL and CNRS to derive temperature profiles have been substantially improved leading to more accurate temperature measurements and over a broader altitude range [Leblanc *et al.*, 1998]. A similar evaluation and optimization study has also been made for the ozone algorithm and all of the raw data from TMF and MLO has been reanalyzed.

In cooperation with the French NDSC Lidar Group (CNRS-SA) and with Colorado State University we have been able to create a temperature climatology of the stratosphere and mesosphere from 19.5° N to 44° N [Leblanc *et al.*, 1998]. The extended data sets in the NDSC database form the basis of this climatology and provide an example of the value of this archive.

During the last three years we have introduced an additional measurement strategy whereby at two separate times each year, e.g., at the equinoxes, we have made observations during the complete night for approximately 10 successive days (weather and instrument permitting). These campaigns have typically produced on the order of 100 hours of measurements each and have been carried out at both TMF and MLO. These large datasets are producing valuable new insight into ozone and temperature variations on short time-scales. We are able to extract the signatures of gravity waves, planetary waves, and diurnal and semi-diurnal earth tides from these profiles [Leblanc *et al.*, 1999]. We expect the results of these studies to be extremely important in improving satellite validations and also in understanding some of the dynamical issues related to ozone and atmospheric change.

The lidar results continue to be used to support and validate other programs. During 1997 and 1998 these include the STRAT and TOTE/VOTE aircraft campaigns [Grant *et al.*, 1998]. JPL lidar data were also provided to aid in the evaluation of long-term SAGE II results as part of the IOC Ozone Assessment. Coordinated measurements were made and results were provided for the 1997 CRISTA2 mission onboard the Space Shuttle. Also, our lidar results were used in the validation of the earlier CRISTA/MAHRSI flight.

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Network for the Detection of Stratospheric Change (NDSC) Mobile Lidar

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Research Objectives

Two separate mobile lidar instruments are operated by the Atmospheric Chemistry and Dynamics Branch; a Stratospheric Ozone Lidar, which measures vertical profiles of ozone, temperature and aerosols from the upper troposphere to the upper stratosphere and above; and the Temperature and Aerosol (AT) Lidar which measures vertical profiles of aerosols from the upper troposphere into the stratosphere, and temperature in the upper troposphere to the mesosphere. Both instruments are housed in their own individual trailers, and are independently transportable and self-contained. Within the Network for the Detection of Stratospheric Change (NDSC), Stratospheric Ozone Lidar provides a transfer calibration standard for permanent ground-based ozone lidars, and is used to validate those instruments at the primary NDSC sites. The Aerosol and Temperature Lidar performs the same function for aerosols and temperature, and also operates at the GSFC NDSC Complementary site. The AT lidar also provides wavelength dependent data for aerosols. Beyond the NDSC functions, these lidars are used for validation of satellite instruments, participating in both UARS and SAGE II correlative measurement programs. The lidars are also used as test beds for new technology to be incorporated into lidar instrumentation.

Summary of Progress and Results

The Ozone Lidar: The Ozone Lidar underwent substantial modification to the data system during this time period. Faster photon counting boards were added to the system, and the acquisition software was rewritten in LabVIEW, resulting in a more efficient data acquisition system. The Ozone lidar has participated in several campaigns during this reporting period:

February - March 1997: The ozone trailer was deployed to Table Mountain, California at the same time that the Stratospheric Aerosol Intercomparison (STRAIT) took place. During this deployment the Ozone lidar was used to test a prototype tropospheric ozone lidar, capable of making measurements during the daylight hours. The tests were successful and the instrument is being incorporated into a laboratory operation.

July-August 1997, Observatoire de Haute Provence (OHP): The ozone lidar participated in a Network for the Detection of Stratospheric Change (NDSC) validation campaign at OHP. The instrument had been at OHP in 1992 and returned as part of the NDSC protocol for continuing validation. The instrument at OHP had been substantially modified during the time since the last validation campaign in 1992. This was a blind intercomparison with Geir Braathan of NILU serving as the independent referee.

January-February 1998: After the OHP campaign, the ozone lidar was transported to Ny Alesund, on the island of Spitsbergen (79N) for a winter Arctic campaign. This also was a NDSC validation campaign for the new lidar and microwave instrumentation at the station. Wolfgang Steinbrecht was the referee for this campaign.

During the shipment to OHP and Ny Alesund and the return, the trailer sustained substantial damage to the exterior. Upon its' return, that damage was repaired and the trailer setup to make measurements at GSFC. It was then discovered that some of the electronics in the data acquisition system and in the lasers themselves, as well as the some of the optics and the optical alignment had also been damaged. The troubleshooting and repairs of these items forced the postponement of campaigns at Toronto and Eureka, Canada until the Summer of 2000.

The AT Lidar: After extensive testing and measurements at Mauna Loa, Hawaii, the AT lidar made measurements of aerosols and temperature above the GSFC Complementary NDSC site, until it was deployed to Table Mountain, California to participate in the Stratospheric Aerosol Intercomparison (STRAIT) campaign in February-March 1997. This was an international comparison among four lidar systems: the GSFC Ozone and AT lidars, the Mobile Aerosol Lidar (MARL) from the Alfred Wegner Institute in Potsdam, Germany, and the Table Mountain Aerosol Lidar (TAL). In addition, backscatter sondes from the University of Wyoming were flown from the observatory. During this time, simultaneous observations of cirrus clouds were made by the four lidars and the backscatter sondes. The data showed very good agreement between the AT lidar data, and the backscatter sonde data. After this campaign the trailer was returned to GSFC and resumed measurements at that site, during the remainder of FY97, and FY98. During FY99, the AT trailer has been used extensively as a test bed for new electronics and for new PMT technology which is being incorporated into the GSFC SOLVE instrument. The new PMT's have proven to perform better than PMT's currently in use on the GSFC lidars, and should allow for the removal of the mechanical choppers now used to prevent signal induced non-linearities in the lidar returns, when the initial signals are very large.

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Measurements of Hydroxyl Column Abundances: Implications for the Photochemistry of the Middle Atmosphere

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Research Objectives

The goal of this research is to improve our understanding of the photochemistry of reactive hydrogen compounds in the Earth's upper atmosphere. In particular, the hydroxyl (OH) radical is one of the most chemically active constituents in the atmosphere. Hydroxyl plays a direct role in the chemical budget of stratospheric ozone and is involved also in reactions between active and stable compounds of chlorine and nitrogen. In the research described here, the vertical column abundance of atmospheric hydroxyl (OH) is measured from ground-based instruments, providing information on the diurnal, seasonal, long term, and geographic behavior of column OH. These are high resolution spectral measurements of the resonance absorption of sunlight in a single electronic line of OH in the ultraviolet, near 308 nm. The observations are a useful diagnostic for constructing and testing atmospheric models used to predict the integrity of stratospheric ozone under changing conditions resulting from anthropogenic emissions.

Summary of Progress and Results

Ground-based measurements of sunlight absorption in the OH P1(1) resonance line at 308 nm have been made on a continuous basis at Fritz Peak, Colorado, using a high resolution, PEPSIOS spectrometer. This is a continuation of the long-term OH database from Fritz Peak which now extends over 22 years. Recent measurements show the persistence of a new regime in OH column abundances compared to previous years, and suggest fundamental changes in the photochemistry of odd-hydrogen in the middle atmosphere. Beginning in 1991, morning OH abundances in the fall season were found to be about 15% lower than the previous 1980-1990 average. The 1997 fall values dropped an additional 15%, and were some of the lowest values found for the entire data period dating to 1977. Abundances for fall 1998 and 1999 indicate a partial recovery to near the long-term average.

A PEPSIOS instrument of identical design is currently operational and has been used since April 1996 for OH column measurements at the New Mexico Institute of Mining and Technology in Socorro, New Mexico. This instrument was relocated to a new building during 1998; observations from New Mexico resumed in January 1999. Comparative measurements from the

two instruments for April 1996 through November 1997 indicate small differences in OH column abundances, with New Mexico (34N latitude) abundances about 10% above Colorado (40N) values for comparable solar zenith angles. Seasonal and secular variations in OH abundances are similar at both locations, with New Mexico data phase lagged by 1-2 months with respect to Colorado OH data.

The NCAR ROSE model has been modified to run in 1-D column mode for comparison with the OH measurements. The model also has been updated with the most recent recommendations for reaction rate constants and photolysis cross sections, as well as heterogeneous chemistry on aerosol distributions based on SAGE II data. Long-lived source gases from UARS HALOE and MLS measurements also have been incorporated into the model. Calculations indicate a discrepancy between modeled and measured OH column abundances for solar zenith angles less than 60 degrees, with model OH lower by 10 to 30%. This pattern appears consistently in all comparisons with previous data from New Zealand, Micronesia, Florida, New Mexico, and Colorado. The discrepancy is nearly absent, however, in the fall 1997 data from New Mexico and Colorado. Work is ongoing to compare model results with empirical OH vertical profiles based on a compilation of OH measurements from aircraft, balloon, and satellite platforms.

Quantification of stray light levels in both PEPSIOS instruments has been investigated using the method of strong solar line absorption as an alternative to the Kitt Peak standard which has been used in the past. We have collaborated with researchers from the University of Tokyo on these studies of instrumental stray light, since this has been suggested as a possible factor in differences between OH data from the two groups. Results indicate no significant problems with stray light determinations in either experiment.

Spectral simulations of the P1(1) OH absorption line have been made to investigate the possibility of constraining the altitudes regions where changes in OH may be taking place. Synthetic spectra have been analyzed using our standard OH retrieval algorithm. These simulations indicate that the retrieval is most sensitive to changes in OH at the mesopause, and to a lesser extent, at the tropopause. In all cases, the retrieved OH column agrees with the simulated input column to within 8%. The results of this and the stray light investigation are being incorporated into a paper, currently in preparation, which reviews the long term OH record and experimental methods.

Collaboration with the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) science team at the Naval Research Laboratory is ongoing. Ground-based data was obtained under this project during the MAHRSI shuttle flight of November 1994, and during an August 1997 mission. We are focusing on comparison of August 1997 ground-based column data with MAHRSI OH profiles between 45 and 80 km. MAHRSI OH profiles from this period includes mid-latitude observations at small solar zenith angles.

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Infrared Measurements of Atmospheric Constituents - Ground Based Observations

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Research Objectives

Very high resolution solar spectrometers provide data on a variety of chemical compounds related to stratospheric ozone chemistry. In 1991, we installed a system at Mauna Loa, Hawaii. In late 1995, the system was replaced with more capable one, which is also automatic. Spectral data are recorded 5 days per week, when weather permits. In 1996 a similar system was installed at Arrival Heights, Antarctica, replacing an old, lower resolution instrument. The spectra are analyzed for total column abundances of CFC-12, CFC-22, HNO₃, N₂O, CH₄, HCl, HF and O₃, which have been placed in the Network for Detection of Stratospheric Change data base. The spectra have also been analyzed for limited vertical profile information for some compounds.

Summary of Progress and Results

The instrument at Arrival Heights, Antarctica did not operate well during the first season, and provided only limited data. It was serviced early in 1997, and produced good data for the austral spring of 1998, and for austral fall 1999. Some test spectra using the Moon as the source (for winter observations) have also been obtained. Some publications have already resulted from these data, because of the rapid changes in chemistry that occur during the ozone hole period. This instrument is operated by personnel from the New Zealand Institute for Water and Air Research.

The Mauna Loa instruments have provided a good set of data for nearly 8 years, beginning soon after the eruption of Mt. Pinatubo which injected large amounts of aerosol into the stratosphere. The aerosol surfaces changed the photochemical balance, and increased the HNO₃ column by about 50%. It took several years for the HNO₃ column to recover.

Maintaining an instrument for long term, high precision measurements is a distinct challenge, and we are beginning to see the results of years of work. The changing trends in the CFCs are clearly discernable, as well as trends in HF and HCl.

Altitude information about a compound is more difficult to extract from the spectra than the total amount, but significant progress is being made, as evidenced in the publications.

Because solar measurements are not possible in winter in the Arctic or Antarctic, we operated an emission spectrometer at the South Pole during 1996, 1997, and 1998. This instrument uses the thermal infrared emission from the atmosphere itself to determine total quantities of gases, particularly HNO₃. During the winter the HNO₃ is almost completely converted to polar stratospheric clouds by late May.

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Ground Based Monitoring of Water Vapor in the Earth's Middle Atmosphere

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Research Objectives

The goal of this task is to provide the first continuous record of water vapor in the middle atmosphere using ground based radiometers. The instruments are installed at sites of the Network for the Detection of Stratospheric Change (NDSC) and provide the sole source of middle atmospheric water vapor data from these sites. Since water vapor is the primary source of the OH radical and other hydrogen compounds, it is important in controlling ozone chemistry. The multi-year data record from these instruments provides an important means of detecting long-term changes in water vapor which may result from increasing levels of methane, changes in stratospheric transport, or changes in stratosphere-troposphere exchange.

Summary of Progress and Results

The Water Vapor Millimeter-wave Spectrometer (WVMS) instruments provide daily measurements of the water vapor profile from 40 to 80 km. All of the instruments have provided nearly continuous data records during their period of operation. The data from Table Mountain, California covers the periods from January to October 1992 and from May 1993 to November 1997. The measurements from Lauder, New Zealand cover the period from November 1992 to May 1993 and from January 1994 to the present. A third instrument was installed at Mauna Loa, Hawaii in February 1996, and has been providing continuous data since that time. The instruments are all operated remotely from the Naval Research Laboratory, with calibration and emergency support provided by on-site staff.

An extensive validation paper in which the water vapor profiles from the WVMS instruments were compared to several satellite based datasets was published in 1997. This showed generally good agreement between most of the existing datasets, with differences <1 ppmv at most altitudes from 40 to 80 km. While up to five nearly coincident measurements were available during the NASA Atmospheric Laboratory for Application and Science (ATLAS) shuttle mission in April 1993, only the WVMS and HALOE instruments have provided water vapor measurements continually since 1992.

The importance of maintaining continuous measurements of water vapor was highlighted by the large increase in middle atmospheric water vapor (1-2%/year) which was observed in the early

1990s. This increase was observed by the ground-based WVMS instruments at Table Mountain and Lauder, and by the Halogen Occultation Experiment (HALOE) aboard the UARS satellite. While there was no reason to distrust the validity of the increase in water vapor observed by HALOE during the early 1990s, the availability of several years of ground-based water vapor measurements from two NDSC sites provided a valuable validation of the results. The measurement of such a large increase from three independent instruments helped not only to confirm the accuracy of the observed increase in water vapor, but also provided added confidence that HALOE measurements of large variations in other species during the early 1990s were accurate.

The increase in middle atmospheric water vapor observed from 1992-1996 prompted considerable interest in the WVMS measurements. The results were included in the WMO Scientific Assessment of Ozone Depletion: 1998, and were reported on in Science News (March 28, 1998). Measurements from Mauna Loa and Lauder since 1996 have not shown the increase observed during the years 1992-1996, and there is even some suggestion of a decrease in middle atmospheric water vapor from 1996-1999, in agreement with the results from HALOE.

In addition to the providing measurements of long-term changes in water vapor, the WVMS instruments continue to provide a valuable measurement of the semi-annual, annual, QBO variations in water vapor. In the mesosphere, where the photodissociation of water vapor makes it sensitive to the solar cycle, the measurements show the effect of increasing Lyman-alpha radiation on water vapor since solar minimum. The mesospheric observations at Table Mountain and Mauna Loa also show the effects of the mesospheric QBO, in good agreement with the variations observed by HALOE.

From March 1996 through November 1997 measurements were available at both the Table Mountain and Mauna Loa sites. This set of coincident measurements provided us with an opportunity to validate instruments at two sites that were physically distinct, but close enough in latitude (34.4°N and 19.5°N) to share many similar variations. A comparison of the difference in the WVMS measurements at these two sites showed a latitudinal variation that was very similar to that of HALOE.

As of September 1999, WVMS instruments continue to operate from Mauna Loa and Lauder. The maintenance of the electronics and cryogenics on these instruments, in order to ensure that the dataset remains as continuous as possible, is one of the most significant accomplishments of this task. Work is also underway to bring the instrument at Table Mountain back into operation. Support from the on-site personnel at all three NDSC sites continues to be excellent, and ensures the accurate calibration of these instruments that is crucial to their use for measurements of multi-year variations.

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NDSC Microwave Ozone Instruments

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Research Objectives

The research objectives are as follows:

- To maintain and calibrate the microwave ozone instruments at Mauna Loa, Hawaii, and Lauder, New Zealand to obtain high quality spectral data with minimal interruptions.
- To retrieve ozone mixing ratio profiles over the range 56-0.1 mb (20-66 km) from the spectra.
- To evaluate the quality of the data, and archive all good data in the NDSC database.
- To work with other investigators working at those sites to evaluate the quality of all ozone data being produced at those sites, and attempt to resolve discrepancies.
- To assist investigators operating satellite-borne instruments in using our microwave data, as requested.
- To interpret the microwave data scientifically.

Summary of Progress and Results

We continue to operate two microwave ozone profiling instruments, one at Lauder, New Zealand, and a second at Mauna Loa, Hawaii. The data record at Lauder began in 1992; at Mauna Loa it began in 1995. Data are recorded continuously in clear weather. There are two gaps of several months in each dataset.

During the last several years, we have concentrated our efforts on developing more sophisticated calibration procedures for, and applying them to the Lauder data. The limiting factor in the precision of our profiles is the measurement of the attenuation of the ozone signal due to water vapor and oxygen in the troposphere. The Lauder NDSC site is at an altitude of 400 meters,

much less than the 2400 meters of the site for which our initial calibration procedures were developed. The tropospheric attenuation at Lauder is therefore both larger and more dependent on the altitude distribution of water vapor and temperature than at a mountaintop site. The upgraded procedures account for seasonal temperature and water vapor variations, and are based on local balloon soundings. Secondly, we discovered, in 1996, that our measurements of an angle needed in the calibration were slightly uncertain. The basis for the angle measurement is a geometrical survey. The 1996 survey showed an unexpected height difference of a calibration device of a few centimeters with respect to the 1992 survey, and independent evidence indicated that foundations for the instrument shelter, calibration device, etc. had heaved or settled. The survey has been repeated 9 times since 1996, and no further motions have been detected. We developed an alternative, independent procedure to obtain the needed angle data, and validated the alternative technique using the post-1996 data.

We have completed a uniform reprocessing of the Lauder microwave data from 1992 through 1998 [Tsou *et al.*, in preparation] incorporating the upgrades discussed above. We have intercompared our measurements with co-located lidar and ozonesonde measurements, and with satellite-borne Stratospheric Aerosol and Gas Experiment II (SAGE-II) and Halogen Occultation Experiment (HALOE) measurements; agreement with lidar and sonde is better than 6% on average, and with SAGE-II and HALOE it is 2-3% on average. Time series of difference profiles do not show significant trends, except possibly near 20 km.

We are presently actively processing the Mauna Loa data from 1997 on; earlier data are in the data base. We expect a high quality data set because the tropospheric attenuation at Mauna Loa is typically much less than at Lauder, and because we have not found any unexpected sources of calibration uncertainty. The microwave profiles agree with SAGE-II and HALOE within 5% from 20 to 52 km, and with co-located JPL lidar profiles within 6% from 20 to 40 km. Samples of our 1998 data continue to show agreement at this level.

We have completed a study [Parrish *et al.*, 1998] of ozone profiles measured with one of our instruments while it was installed at Table Mountain, California during the years 1989-1992, which included the June 1991 Pinatubo eruption. This work included lidar aerosol measurements. We failed to detect any detailed anti-correlation between ozone and Pinatubo aerosol levels. However, we did measure a significant decline in ozone in the 20-24 km range beginning in November 1991, when the Pinatubo aerosols became well established, reaching 11-15% in June 1991. The observed depletion was greater than predicted by models.

We have investigated the annual and seasonal ozone variations which we have observed in the six year Lauder data record described above, and have found that they were generally consistent with expected variations caused by photochemical and dynamic processes. However, we observed an exception in the upper stratosphere during the winter of 1995, when low ozone values were observed in the absence of an upper stratospheric warming which is the usual cause for winter ozone decreases. In this instance, measurements of long lived methane and potential vorticity analyses support the hypothesis that transport of ozone-poor polar air over Lauder caused the low ozone values. These results are discussed in Tsou *et al.* (in preparation).

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Advanced Global Atmospheric Gases Experiment (AGAGE)

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Research Objectives

Continuous high frequency *in situ* gas chromatographic FID/ECD measurements of two biogenic/anthropogenic gases (CH_4 , N_2O) and five anthropogenic gases (CFCl_3 , CF_2Cl_2 , CH_3CCl_3 , $\text{CF}_2\text{ClCFC}_2$, CCl_4) are carried out at five globally distributed sites (Ireland, California, Barbados, Samoa, Tasmania). Also, high frequency *in situ* gas-chromatographic mass-spectrometric measurements of about 30 species including chlorofluorocarbon replacements and many natural halocarbons are made at two sites (Ireland, Tasmania). Finally, high frequency *in situ* gas chromatographic HgO-RD measurements of CO and H_2 are performed at two sites (Ireland, Tasmania). The goal is quantitative determination of the sources, sinks, and circulation of these environmentally important gases.

Summary of Progress and Results

The accomplishments of AGAGE under this grant over the period 1997-1999 have been substantial and are documented in a large number of peer-reviewed publications. The data for the many species measured in AGAGE are generally of high quality and are recorded in public archives. In this section we provide a summary of our research highlights for the past two years.

GAGE/AGAGE measurements of CFCl_3 indicate its global concentrations reached a maximum in 1993 and decayed slightly after that, while CF_2Cl_2 levels continued to increase but only slowly since 1993 [Cunnold *et al.*, 1997; Prinn *et al.*, 1999]. Analysis of regional pollution events in Ireland suggest that industry estimates of the rate of decline in European emissions are too small [Derwent *et al.*, 1998a]. Measurements of CCl_4 from July 1978 to June 1995 show a maximum in its global concentration in 1990, followed by a small decrease since then [Simmonds *et al.*, 1998a]. GC-MS measurements of $\text{CF}_3\text{CH}_2\text{F}$, CCl_2FCH_3 , and CF_2ClCH_3 (HFC-134a; HCFCs 141b and 142b) at Mace Head indicate rapid increases in the levels of these CFC replacements, and that industry estimates of HCFC-141b and particularly HCFC-142b emissions appear far too small to explain the observations [Simmonds *et al.*, 1998b]. Measurements of CHClF_2 (HCFC-22) in the Cape Grim archive and at La Jolla have been used to estimate OH concentrations and this yields values larger than those determined from CH_3CCl_3 (but due to the larger uncertainty in the HCFC-22 based estimate the difference is not statistically significant [Miller *et al.*, 1998]). A

Lagrangian dispersion model has been used to analyze 1996 Mace Head observations showing North American sources occasionally produce pollution events at this station, which are about 10% of those due to the European sources [Ryall *et al.*, 1998]. Mace Head data for CH₄, N₂O, and CO₂ have been analyzed to elucidate European and Northern-Hemispheric sources [Derwent *et al.*, 1998b]. A complete description of instrumentation, calibration, and observations over the entire ALE/GAGE/AGAGE experiment together with model-based back-extrapolations has yielded a complete definition of the history of ozone-depleting manmade halocarbons in air [Prinn *et al.*, 1999]. Several AGAGE scientists were lead or co-authors in the recently completed 1998 Ozone Assessment [Kurylo *et al.*, 1999; Prinn *et al.*, 1999].

The AGAGE instruments for the measurement of CCl₃F, CCl₂F₂, CCl₂FCClF₂, CHCl₃, CH₃CCl₃, CCl₄, N₂O and CH₄ at the five AGAGE clean air measurement sites and at the Scripps Institution of Oceanography (SIO) calibration laboratory and measurement site have continued to operate with unprecedented precision, frequency and reliability throughout the past two years. Also, the second AGAGE GC-MS system was prepared at Bristol University and installed at Cape Grim Tasmania in November 1997, where it is operating successfully. A third system at Bristol University is being used to prepare new standards for the GC-MS gases and the SIO group is working with the Bristol group to develop a new generation of cryo-trapping and injection techniques for improved GC-MS accuracy and calibration versatility. AGAGE primary calibration work has continued to advance, with the completion of the more accurate SIO-1998 calibration scale. This has included all of the halocarbon compounds analyzed by the AGAGE multi-detector GC system, as well as a new primary N₂O standard which is free of the contaminants which biased the earlier SIO-1993 halocarbon calibrations. SIO is continuing its calibration work on selected compounds measured by GC-MS and by oxygen-doped ECD, including CHClF₂, CH₃Br, CH₃Cl and SF₆, and is continuing to participate actively in intercalibration exercises with other laboratories. The entire ALE/GAGE/AGAGE GC-ECD data base comprising every calibrated measurement including pollution events from June 1978 through March 1998 is publicly accessible at the Carbon Dioxide Information and Analysis Center (CDIAC) at the U.S. Department of Energy, Oak Ridge National Laboratory, through the Internet at <http://cdiac.esd.ornl.gov/ndps/alegage.html>.

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UV/Visible Interferometry

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Research Objectives

The overall objective of this work is to provide measurements and model interpretation of several trace species important in atmospheric ozone chemistry including O₃, NO₂, NO₃, BrO, and OH using the techniques of high-resolution UV-visible interferometry and grating spectroscopy. Measurements of the diurnal and seasonal variations and long-term trends of the OH column density, when combined with measurements of H₂O, O₃, CH₄ and solar radiation from satellite and ground-based instruments, will provide a critical test of the ability of atmospheric models to reproduce the vertical profile and long-term trends of O₃ in the middle and upper stratosphere. Significant discrepancies between models and measurements of O₃ production and loss in this altitude region have persisted despite recent significant improvements in the quantity and quality of global measurements, and in the accuracy of kinetic and photochemical parameters. Another important objective of this program is the measurement of NO₃ column densities to provide ground-based validation for upcoming measurements by the SAGE III satellite instrument. NO₃ is a key intermediate in the nighttime conversion of NO₃ to N₂O₅ and HNO₃ in the lower stratosphere. This important process has a significant effect on the partitioning of NO_x and the budget of HO_x.

Spectroscopic measurements in the UV-visible spectral region are made using the FTUVS spectrometer and a grating spectrometer, which are deployed at JPL's Table Mountain Facility, near Wrightwood, California.

Summary of Progress and Results

Measurements of the Column Abundance of OH: A continuous data record of the OH column abundance has been obtained beginning in August 1997. At this writing, there are approximately 125 days of data in the OH data record. Data quality from the FTUVS spectrometer is excellent. Measurements are obtained over a full diurnal cycle, and acceptable data are obtained for solar zenith angles less than about 75 degrees.

In support of our modeling work on OH and other molecules, we are collaborating with the research group of Professor Yuk Yung at Caltech. With the assistance of Professor Yung and co-workers, the Caltech/JPL 1-D model is being adapted for the analysis of our OH column data. This involves carrying out a sensitivity analysis to determine which model parameters influence column OH, then assimilating data from UARS, the NRL water vapor radiometer at TMF and the JPL O₃ lidar at TMF into the model. The modeling work is making satisfactory progress, and we expect to submit a manuscript for publication during FY99.

Measurements of NO₃: Activities over the past year have been aimed at improving the measurement capability for NO₃ and developing a new capability for NO₂. For measurements of NO₃ we have set up a grating spectrograph/diode array detector instrument in addition to the interferometric spectrometer as described above. This instrument records absorption spectra over a 55 nm spectral interval centered at 662 nm with a spectral resolution of 0.43 nm. With this instrument the time required to obtain a lunar spectrum under clear-sky conditions is typically 15 s. The minimum detectable absorbance is typically a few parts in 10⁴. Four spectra are averaged for each acquisition. The reference spectrum is a solar spectrum or a lunar spectrum after sunset before substantial NO₃ buildup has occurred.

An important aspect of the NO₃ retrieval is the proper correction for the water vapor interference. This is complicated by the highly variable nature of the tropospheric water vapor distribution and the sensitivity of the spectral band shape to this distribution. In our forward model, two line-by-line spectral simulation codes (LBLRTM, Clough *et al.*, and an in-house code, Nemtchinov *et al.*) were intercompared using the HITRAN line parameters for water vapor in the 640-665 nm spectral region. The model used a water vapor profile based on balloon sonde hygrometer soundings. While the forward model captures most of the observed spectral features, the residuals in the water vapor band are still fairly large. We have concluded that the residuals are due primarily to errors in the assumed water vapor vmr profile, and with possible errors in the HITRAN line parameters. We are investigating the use of a retrieval code which will optimize the water vapor fits with the use of a model atmosphere with 3-5 vertical levels (2-4 levels in the troposphere, 1 in the stratosphere). In addition, laboratory investigations are underway elsewhere to improve the accuracy of the water vapor line list.

Lunar measurements using the grating spectrometer began in November 1998 and have continued through each subsequent full moon opportunity. NO₃ can be successfully measured with excellent temporal resolution starting immediately after sunset when NO₃ levels are near their minimum values. Large variability in the observed measurements has been observed. Some of this variability is due to tropospheric NO₃ which is influenced by the NO_x sources within the Los Angeles area. The precision and accuracy of these retrievals are currently being assessed.

Measurements of NO₂: We have discovered recently that we can easily make daytime measurements of NO₂ column densities. Since NO₂ is one of the key scientific objectives of both NDSC and the SAGE III Validation Program, these measurements will hopefully complement our existing efforts on behalf of UARP.

The NO₂ measurements are carried out using the FTUVS interferometer operating at a spectral resolution of 0.05 cm⁻¹ (0.0009 nm). At this resolution, NO₂ vibronic features can be seen clearly at wavelengths near 425 nm. The atmospheric spectrum is broadened compared with laboratory reference spectra obtained at the same resolution most likely because of pressure broadening. This suggests that the NO₂ vertical profile can be retrieved, perhaps with a resolution of 1-2 scale heights. Because there are a few segments of the NO₂ spectrum that occur where there are no measurable solar lines, the NO₂ measurements can be performed without the need to ratio against a reference spectrum. The NO₂ features can be observed clearly at solar zenith angles which exceed about 60 deg. Reference spectra for NO₂ covering the relevant atmospheric pressure and temperature ranges are not currently available at this resolution. This represents an important need area in order to interpret these measurements fully.

Publications

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Ground-Based Measurements of Stratospheric ClO as Part of the Network for Detection of Stratospheric Change (NDSC)

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Research Objectives

Chlorine oxide, ClO, is the principal chemical involved in the catalytic destruction of ozone by chlorine from CFCs and other man-made chemicals. The objective of this research is to measure the content and distribution of stratospheric ClO from ground-based stations using the technique of millimeter-wave spectroscopy. This is the same technique we previously employed to make the first measurements of a huge excess of ClO in Antarctica during the National Ozone Expedition in 1986. This work is in close collaboration with Alan Parrish of Millitech Corporation, who built the instruments, and, for the Antarctic work, with Brian Connor of New Zealand's National Institute of Water and Atmospheric Research (NIWA). The goals for this project are:

- To monitor the ClO content of the atmosphere on a long-term basis using our instruments at Mauna Kea, Hawaii, and Scott Base, Antarctica, as part of the NDSC. Data acquisition is monitored and controlled from SUNY at Stony Brook. The data are downloaded daily to Stony Brook where they are stored and processed.
- To obtain altitude profiles of ClO from 16 to 47 km to be used as part of a complete picture of the stratosphere. These measurements can be used as a test of models of stratospheric chemistry, a process we have already begun using our Antarctic data.
- Comparison of ground-based with space-based measurements of ClO, such as those made the Upper Atmosphere Research Satellite (UARS) and any future missions. These ground-based instruments will also be the major source of complete altitude profiles of ClO if space-based instruments cease operations.
- Intercomparisons of the three ground-based millimeter-wave ClO instruments built by Millitech to check for consistent calibration. This has now been successfully completed.

Summary of Progress and Results

Antarctic Site, Scott Base: In collaboration with NIWA, one of the Stony Brook-NDSC instruments installed at Scott Base (latitude -77.85°), part of the NDSC's Antarctic Station. It began producing useful data in February 1996, and, except for downtime due to equipment problems in November 1996 to February 1997 and April-June 1998, has been in continuous

operation since. It was thus able to observe the development of the ClO altitude distribution during the Antarctic ozone holes of 1996, 1997, and 1998, and the first data on the 1999 hole are coming in as this is written.

The onset of ClO in the lower stratosphere is strikingly similar in all three years. From August 13 and September 4, the ClO mixing ratio at 22 km rises from 0.1 ppbv to 1.9-2.0 ppbv, and the column density above 15 km rises from 0.0 to $2.2 \times 10^{15} \text{ cm}^{-2}$ (Note that these values represent the difference between the daytime and much smaller nighttime levels of ClO). The shape of the increase is similar from year to year. After September 7, each year is different due to the varying location of Scott Base with respect to the vortex and to differences in the activation of the air parcels following the almost complete depletion of ozone in layers dominated by heterogeneous chemistry. In 1997 and 1998, the chlorine remained largely in active form until about September 29, while in 1996 there was a rapid and sharp decline in ClO beginning on September 12.

We have compared our 1996 data to a matched 3-dimensional model simulation provided by the Cambridge (UK) Centre for Atmospheric Science. There is excellent agreement between the model and measurements in the rate of increase of ClO from August 12 to August 28, but the model ClO column is lower than the measurements by $2 \times 10^{14} \text{ cm}^{-2}$. This may indicate that the model's rates for photolysis of the ClO dimer by long wavelengths are too slow. If so, this would have important implications for calculation of ozone depletion rates. Both model and measurements level off during late August to mid-September, depending on altitude, and the peak mixing ratios agree extremely well. Both the model and measurements show a very sharp drop in ClO from September 12 to 15, more rapid and severe in the data. Potential vorticity maps show that Scott Base was briefly outside the vortex (or on the very edge) on September 15, which had the lowest measured ClO over the entire period. The model successfully predicts the lower ClO mixing ratios during the last half of September, due primarily to partial return of Cl into inactive species (HCl, ClONO₂). Similar comparisons will be done for other years when the model results become available.

Hawaiian Site - Mauna Kea: Current measurements show middle (30 to 45 km) stratospheric ClO concentrations 45% higher in 1996 than in 1983. This is in good agreement with the increase expected from models of CFC production and transfer into the stratosphere.

The Mauna Kea instrument was down during October 1998 to March 1999, due to problems with its cryogenic system, but otherwise has continued to produce high quality data

The French ClO instrument, normally based at the Plateau de Bure, was brought to Hawaii and intercompared with the Mauna Kea Stony Brook-NDSC instrument during November 1996 to April 1997, with good results.

Publications

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D. AIRCRAFT-BORNE MEASUREMENTS

Airborne Measurements of Aerosol Parameters and Trace Gas Species for the SAGE III Ozone Loss and Validation Experiment

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Research Objectives

Our group will provide *in situ* measurements of aerosol parameters along with dew point and ozone aboard the NASA DC-8 during the SAGE-III Ozone Loss and Validation Experiment (SOLVE). The fast-response (~1 Hz) suite of instruments will include: condensation nuclei counters to determine the number and size of aerosols between 0.004 and 0.1 μm and the volatility of aerosols $>0.015 \mu\text{m}$; two different aerosol scattering spectrometer probes for obtaining particle size distributions over the 0.1 to 20 μm size range; a cryogenic hygrometer to determine dew points down to -90°C ; and a chemiluminescence instrument to provide O₃ mixing ratio data. The aerosol instruments provide an overall precision of ~5%, whereas the dew point and O₃ measurements are precise to about 0.3°C and 1 ppbv, respectively. The work will include pre-mission instrument calibrations, in-the-field as well as post-mission data archiving, and subsequent data analyses to be performed in collaboration with other investigative groups.

Summary of Progress and Results

Funding for this project began in mid-calendar year 1999. Work to date has included accurate calibration and characterization of the O₃, aerosol and dew point instruments. These have now been integrated into the flight rack scheduled to be shipped to Dryden on October 15, 1999. A team will be dispatched on October 18, 1999 to begin integration of the instruments onboard the DC-8.

Publications

None

Clouds and Water Vapor in the Climate System: Remotely Piloted Aircraft and Satellites

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Research Objectives

The objective of this work is to attack unanswered questions that lie at the intersection of radiation, dynamics, chemistry, and climate. Considerable emphasis is placed on scientific collaboration and the innovative development of instruments required to address these scientific issues. The specific questions addressed include: *Water Vapor Distribution in the Tropical Troposphere*: An understanding of the mechanisms that dictate the distribution of water vapor in the middle-upper troposphere; *Atmospheric Radiation*: In the spectral region between 200 and 600 cm^{-1} that encompasses the water vapor rotational and continuum structure, where most of the radiative cooling of the upper troposphere occurs, there is a critical need to test radiative transfer calculations using accurate, spectrally resolved radiance observations of the cold atmosphere obtained simultaneously with *in situ* species concentrations; *Thin Cirrus*: Cirrus clouds play a central role in the energy and water budgets of the tropical tropopause region; *Stratosphere-Troposphere Exchange*: Assessment of our ability to predict the behavior of the atmosphere to changes in the boundary conditions defined by thermal, chemical or biological variables; *Correlative Science with Satellite Observations*: Linking this research to the developing series of EOS observations is critical for scientific progress.

Summary of Progress and Results

The Interferometer for Emission and Solar Absorption (INTESA), developed under this research support, is an infrared spectrometer designed to study radiative transfer in the troposphere and lower stratosphere from a NASA ER-2 aircraft. The Fourier transform spectrometer (FTS) operates from 0.7 to 50 μm with a resolution of 0.7 cm^{-1} . The FTS observes atmospheric thermal emission from multiple angles above and below the aircraft. A heliostat permits measurement of solar absorption spectra. The calibration system includes three blackbodies to permit in-flight assessment of radiometric error. In the laboratory, the radiometric accuracy is $\sim 0.1 \text{ K}$ in the mid-infrared, an important goal for climate observation from space.

Remote sounding of atmospheric temperature profiles, which is of paramount importance to numerical weather forecasting, has been conducted routinely with the 15 μm CO_2 band using low spectral resolution satellite remote sensors. Next generation atmospheric sounders, such as the Atmospheric Infrared Sounder (AIRS, [Aumann and Pagano, 1994]), is also designed to use the 15 μm CO_2 band, but in addition will have spectral channels in the 4.3 μm CO_2 R branch. This

region is useful because the weighting functions are quite sharp (partially due to the lack of interfering hot bands and isotopes) and because the Planck function is more sensitive to the temperature in the short wave. AIRS has a nominal spectral resolution of 2 cm^{-1} in this region, thus producing a good number of channels with sharp weighting functions.

Like remote sounding using the $15\text{ }\mu\text{m CO}_2$ band, implementation of the $4.3\text{ }\mu\text{m}$ band sounding requires an accurate forward transmittance model for temperature retrieval. The well-known extreme sub-Lorentz behavior of the CO_2 lineshape in this region is difficult to model, especially inside the bandhead between lines, which is where the best sounding channels are located. Moreover, there are very few studies of the lineshape at low temperatures relevant for atmospheric sounding. Thus, validation of forward model assumptions with in-flight measurements is an important step toward improvements of model and temperature retrieval.

We present our approach and preliminary findings from a recent field campaign using a newly developed high-resolution Interferometer for Emission and Solar Absorption (INTESA) flown on the NASA ER-2. The observed radiances and transmittances are compared to computed quantities using a new pseudo line-by-line algorithm, kCARTA [Strow *et al.*, 1998]. kCARTA uses compressed look-up tables for computation of transmittances and radiances that were derived from the GENLN2 line-by-line code [Edwards, 1992], which uses a parameterization of the $4.3\text{ }\mu\text{m CO}_2$ lineshape developed by Cousin *et al.* [1985].

The character of the data required to measure decade-to-century scale climatic change is distinctly different from that required for weather prediction or for studies of meteorological processes. The data must possess the accuracy to detect the small secular climate changes of interest. To be useful to future investigators, the data must include convincing proof that a given level of accuracy was in fact attained. An approach founded on the over-determination of instrument calibration, an approach that aims to reveal rather than conceal instrumental error, is shown to be capable of providing convincing accuracy.

Spectrally resolved infrared-radiance is arguably the single most important quantity to measure accurately from space—it contains the fingerprint of both climate response and the forcing that causes it. Kiehl [1983] showed that IR radiance observations could be used directly to detect the climatic response to greenhouse gas forcing. Haskins *et al.* [1999] have demonstrated that IR-radiances can be used to construct powerful tests of the fidelity of climate models. They compare the vertical covariance in temperature and water-vapor predicted by a model with observations of this covariance via a comparison between predicted and observed radiance covariances. By using raw radiance data directly, these methods provide the ability to test models against data that are uncontaminated by a retrieval system.

Enhanced stratospheric ozone depletion in the polar vortices depends on the persistence of temperatures sufficiently low to allow heterogeneous reactions on cold aerosols. Both the temperature of the vortex and the temperature below which these reactions become important depend on the concentration of water vapor, which is determined by the mean mixing ratios of H_2O and CH_4 entering the stratosphere in the tropics ($[\text{H}_2\text{O}]_e$ and $[\text{CH}_4]_e$). Recent work shows that $[\text{H}_2\text{O}]_e$ is well predicted by the mean saturation mixing ratio of water vapor at the tropical tropopause. While temperatures in most of the stratosphere will cool as greenhouse gas concentrations increase, the tropical tropopause may warm, increasing the saturation mixing ratio and thus $[\text{H}_2\text{O}]_e$. Several recent studies have predicted substantial increases in arctic ozone

depletion due to the stratospheric cooling induced by increasing CO₂ concentrations. Here we combine GCM predictions of tropical tropopause temperatures with one-dimensional radiative convective model results, recent progress in understanding the stratospheric water vapor budget, modeling of heterogeneous reaction rates and GCM modeling of the radiative impact of increased water vapor to evaluate the effects of greenhouse gas increases on stratospheric water vapor and thus on ozone depletion. Thus, it is shown that ozone loss in the late winter and spring arctic vortex depends critically on water vapor variations forced by sea surface temperature changes in the tropics.

Publications

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In Situ Detection of OH, HO₂, ClO, BrO, NO₂, ClONO₂, H₂O and O₃ from the ER-2

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Research Objectives

The national research effort in pursuit of an understanding of secular trends in the Earth system and the mechanisms that control those changes centers on four key areas: *Seasonal to Interannual Climate Variability; Climate Change Over Decades to Centuries; Changes in Ozone, UV Radiation, and Atmospheric Chemistry; Changes in Land Cover and in Terrestrial and Aquatic Ecosystems* (see *Our Changing Planet: An Investment in Science for the Nation's Future*). This research is directed primarily at the third national objective—an understanding of the processes that control the production and destruction rate of ozone in Earth's atmosphere and of the production and removal of photochemical oxidants in general from the atmosphere. As such, the research is focused on mechanisms, on photochemical processes, on free radicals, on observational strategies, on interpretive calculations and models, and on airborne missions.

Summary of Progress and Results

The past five years have witnessed dramatic changes in the scientific view of chemically induced changes to the ozone/climate issue. First, the erosion of ozone in the high latitude winter-spring season has grown rapidly worse to the degree that the region is beginning to emulate the Antarctic. Second, the erosion of ozone over mid latitudes in the Northern Hemisphere has been defined in terms of decade-scale changes and the decay rate is on the order of 10% per decade. Third, it is clear that ozone loss rates are sensitively tied to changes in both temperature and stratospheric water vapor mixing ratio. The research that is summarized here centers around a dissection of high latitude chemical loss processes of stratospheric ozone and the coupling of chemistry, radiation, dynamics and climate with emphasis on the UARP Photochemistry of Ozone Loss in Arctic Region In Summer (POLARIS).

- We use the first simultaneous *in situ* measurements of ClONO₂, ClO, and HCl acquired using the NASA ER-2 aircraft during the POLARIS mission to test whether these three compounds quantitatively account for total inorganic chlorine (Cl_y) in the lower stratosphere in 1997. We find (ClO + ClONO₂ + HCl)/Cl_y = 0.92 ± 0.10, where Cl_y is inferred from *in situ* measurements of organic chlorine source gases. We find no evidence in support of missing inorganic chlorine species that comprise a significant fraction of Cl_y. We apply the analysis to earlier ER-2 observations dating from 1991 to investigate possible causes of previously observed discrepancies in the inorganic chlorine budget. Using space shuttle, satellite,

balloon, and aircraft measurements in combination with ER-2 data, we find that the discrepancy is unlikely to have been caused by missing chlorine species or an error in the photolysis rate of chlorine nitrate. We also find HCl/Cl_y is not significantly controlled by aerosol surface area density in the lower stratosphere [Bonne *et al.*, 1999].

- The first *in situ* measurements of ClONO₂ in the stratosphere, acquired using the NASA ER-2 aircraft during the POLARIS mission, are combined with simultaneous measurements of ClO, NO₂, temperature, pressure and the calculated photolysis rate coefficient (J_{ClONO_2}) to examine the balance between production and loss of ClONO₂. The observations demonstrate that the ClONO₂ photochemical steady state approximation, $[\text{ClONO}_2]^{\text{PSS}} = k \times [\text{ClO}] \times [\text{NO}_2]/J_{\text{ClONO}_2}$, is in good agreement with the direct measurement, $[\text{ClONO}_2]^{\text{MEAS}}$. There is no evidence in support of a pressure-dependent quantum yield for photodissociation of ClONO₂ at wavelengths >300 nm. These measurements confirm the mechanism by which active nitrogen (NO_x = NO + NO₂) controls the abundance of active chlorine (Cl_x = ClO + Cl) in the stratosphere [Stimpfle *et al.*, 1999].
- Simultaneous observations of [ClONO₂], [HCl], [OH], [O₃], [CH₄], [NO], and [NO₂], provide the basis for a quantitative examination of gas-phase inorganic chlorine partitioning. As a foundation for the analysis, a method for estimating time constants is developed and used to improve steady-state methodology. This approach reveals the effects of latitude, season, and altitude on Cl_y partitioning and demonstrates that the time constant for chlorine partitioning is 5-15 days during the spring and summer. An integrated photochemical model that is constrained by measured [OH] demonstrates that currently accepted photochemistry overpredicts measured [ClONO₂]/[HCl] by approximately 60% at temperatures near 230 K [Voss *et al.*, 1999].
- Extensive measurement campaigns by the NASA ER-2 have yielded a pole-to-pole database of the species that control HO_x (OH + HO₂) chemistry. The wide dynamic range of these *in situ* measurements provides an opportunity to demonstrate empirically the mechanisms that control the HO_x system. Measurements in the lower stratosphere show a remarkably tight correlation of OH concentration with Solar Zenith Angle (SZA). This correlation is nearly invariant over latitudes ranging from -70°S to 90°N and all seasons. Calculations using *in situ* measurements show that the production rate of OH is proportional to O₃ and ultraviolet radiation flux and the loss rate is proportional to the concentration of NO_y (reactive nitrogen). Changes in the partitioning within NO_y have a dramatic effect on the production and loss rates of HO_x, but little or no impact on the measured abundance of OH [Hanisco *et al.*, 1999].
- *In situ* observations of OH and HO₂ from the Airborne Southern Hemisphere Ozone Experiment (ASHOE)/Measurements for Assessing the Effects of Stratospheric Aircraft (MAESA), Stratospheric Tracers of Atmospheric Transport (STRAT), and POLARIS NASA ER-2 field campaigns are used to examine the partitioning of HO_x in the lower stratosphere and upper troposphere. These measurements span a latitude range of 70°S to 90°N and a variety of atmospheric conditions as a result of seasonal changes and/or altitude. The response of the observed HO₂/OH to changes in temperature and the concentrations of O₃, CO, NO, ClO, and BrO is investigated. The measured ratio is accurately described (within ~± 10%) by a steady state model constrained by the measured mixing ratios of O₃, CO, NO, ClO, and BrO. Given that the concentration of OH has been observed to be a simple function of solar zenith angle in the lower stratosphere, the concentration of HO₂ is controlled by

variability in the species that control the ratio of HO₂ to OH. The response of HO_x to changes in NO_x and O₃ is demonstrated [Lanzendorf *et al.*, 1999].

- Measurements of the concentrations of OH and HO₂ (HO_x) in the high-latitude lower stratosphere imply the existence of unknown photolytic sources of HO_x. The strength of the additional HO_x source required to match the observations depends only weakly on solar zenith angle (SZA) for 80° < SZA < 93°. The wavelengths responsible for producing this HO_x must be longer than 650 nm because the flux at shorter wavelengths is significantly attenuated at high SZA by scattering and absorption. Provided that the sources involve only a single photon, the strength of the bonds being broken must be <45 kcal mole⁻¹. We speculate that peroxy nitric acid (HNO₄) dissociates after excitation to an unknown excited state with an integrated band cross section of 2–3 × 10⁻²⁰ cm² molec⁻¹ nm (650 <λ <1250 nm) [Wennberg *et al.*, 1999].
- The generation of sulfuric acid aerosols in aircraft exhaust has emerged as a critical issue in determining the impact of supersonic aircraft on stratospheric ozone. It has long been held that the first step in the mechanism of aerosol formation is the oxidation of SO₂ emitted from the engine by OH in the exhaust plume. We report *in situ* measurements of OH and HO₂ in the exhaust plumes of a supersonic (Air France Concorde) and a subsonic (NASA ER-2) aircraft in the lower stratosphere. These measurements imply that reactions with OH are responsible for oxidizing only a small fraction of SO₂ (2%), and thus cannot explain the large number of particles observed in the exhaust wake of the Concorde [Hanisco *et al.*, 1997].
- In an effort to better constrain atmospheric water vapor mixing ratios and to understand the discrepancies between different measurements of water vapor in the stratosphere and troposphere, we have carefully examined data from the Harvard Lyman-α photofragment fluorescence hygrometer, which has flown on the NASA ER-2 aircraft during the SPADE, CEPEX, STRAT and POLARIS missions. The instrument is calibrated in the laboratory before and after each deployment, and the calibration is checked by direct absorption measurements in the troposphere and lowermost stratosphere. On certain flights, the ER-2 flew level tracks in which water vapor varied by up to 80 ppmv, under nearly constant atmospheric conditions. These flights provide a stringent test of our calibration via direct absorption, and indicate agreement to within 3% [Hintsa *et al.*, 1999].
- We use *in situ* measurements taken on the NASA ER-2 aircraft during the STRAT mission in 1995 and 1996 with observed CO profiles and a simple photochemical model to calculate the elapsed time between the entry of air into the stratosphere and the observation, which we define as the photochemical age of the air. Using this age as the transit time of the air mass from the tropical tropopause to its measured altitude, we demonstrate that boundary condition values of CO₂ derived from *in situ* measurements from 400–480 K and the photochemical model match reasonably well the boundary condition derived from a fit to CO₂ measurements made very close to the tropopause. For water vapor, the agreement is comparable, where saturation mixing ratios derived from monthly-averaged radiosonde temperatures at the tropopause between 10°S and 10°N provide the proposed boundary condition [Weinstock *et al.*, 1999].
- The origin of air in the lowermost stratosphere is investigated with measurements from the NASA ER-2 aircraft. Air with high water vapor mixing ratios was observed in the

stratosphere at $\theta \sim 330\text{-}380$ K near 40°N in May 1995, indicating the influence of intrusions of tropospheric air. Assuming that observed tracer-tracer relationships reflect mixing lines between tropospheric and stratospheric air masses, we calculate mixing ratios of H_2O (12-24 ppmv) and CO_2 for the admixed tropospheric air at $\theta = 352\text{-}364$ K. Temperatures on the 355 K surface at $20\text{-}40^\circ\text{N}$ were low enough to dehydrate air to these values. While most ER-2 CO_2 data in both hemispheres are consistent with tropical or subtropical air entering the lowermost stratosphere, measurements from May 1995 for $\theta < 362$ K suggest that entry of air from the mid latitude upper troposphere can occur in conjunction with mixing processes near the tropopause [Hintsa *et al.*, 1998].

- Simultaneous, high-resolution observations of ClO , H_2O , tropopause height, particle reactive surface area, and ice saturation occurrence frequency obtained from the NASA ER-2 aircraft are presented. The objective is to test the hypothesis that the existence of cirrus clouds or cold aerosols in the first few kilometers above the tropopause at mid latitudes is responsible for increasing the ratio of chlorine free radicals to total inorganic chlorine, thus amplifying the rate of catalytic ozone destruction. The observations reveal a sharp decrease in ice saturation frequency at the tropopause, a marked degree of under-saturation just above tropopause, a corresponding sharp gradient in the product of cold aerosol reactive surface area and reaction probability, γS_a , and, finally, the consistent absence of enhanced concentrations of ClO immediately above the tropopause. These results suggest that mid latitude ozone erosion is not controlled *in situ* by the mechanism of cirrus cloud and/or cold aerosol enhancement of chlorine radicals in the vicinity of the tropopause [Smith *et al.*, 1999].

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Trace Gas Measurements for Whole-Air Sampling

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Research Objectives

Our research objectives for 1997-1999 were: (1) continue to refine our calibrations of various organic halogens and hydrocarbons, (2) participate in the POLARIS campaign, (3) continue data analysis from the STRAT and POLARIS campaigns, (4) modify the Whole Air Sampler for deployment in the centerline drop tank for the 2000 SOLVE missions, (5) add N₂O to our list of measured compounds for SOLVE, (6) characterize distributions of short-lived halocarbons and hydrocarbons in the upper troposphere/lower stratosphere tropics and mid-latitudes, (7) evaluate transport rates calculated from halocarbon distributions, and (8) characterize and quantify the speciation of organic bromine in the upper troposphere/lower stratosphere.

Summary of Progress and Results

Our laboratory work involved assessments and refinements of calibrations for compounds previously measured in whole air samples as well as for the short-lived trace gases measured during the STRAT, POLARIS, and ACCENT campaigns. Calibration of all species is an ongoing process that involves standard preparations using both static and flow dilution systems. We also participated in successful intercalibrations for several halocarbons with the NOAA Climate Monitoring and Diagnostics Laboratory (including intercomparisons with the ACATS and LACE instruments). For analysis of samples from the STRAT, POLARIS, and ACCENT flights we used the following instrumentation: a GC/MSD (also used on earlier NASA missions), a GC/NICI/MS (for high sensitivity analysis of bromo- and iodocarbons), a redesigned GC/FID instrument (for high sensitivity C2 - C5 NMHC analysis), and a second GC/FID instrument for methane analysis. These instruments will also be used for analysis of the SOLVE samples in addition to a GC/ECD for high precision analysis of N₂O.

The Whole Air Sampler was modified for POLARIS to fit in the center section of the right superpod. A sampling manifold of 29 canisters, a 4-stage metal bellows pump, and control electronics package was built and flown during POLARIS. The Whole Air Sampler was also modified for SOLVE to fit 32 canisters into the centerline drop tank.

Our data analysis involved both tropospheric and stratospheric data sets. A comprehensive suite of brominated organic compounds was measured from whole air samples collected during the 1996 NASA Stratospheric Tracers of Atmospheric Transport aircraft campaign and the 1996 NASA Global Tropospheric Experiment Pacific Exploratory Mission-Tropics aircraft campaign.

Measurements of individual species and total organic bromine were utilized to describe latitudinal and vertical distributions in the troposphere and lower stratosphere, fractional contributions to total organic bromine by individual species, fractional dissociation of the long-lived species relative to CFC-11, and the Ozone Depletion Potential of the halons and CH₃Br. Spatial differences in the various organic brominated compounds were related to their respective sources and chemical lifetimes. The difference between tropospheric mixing ratios in the Northern and Southern Hemispheres for halons was approximately equivalent to their annual tropospheric growth rates, while the interhemispheric ratio of CH₃Br was 1.18. The shorter-lived brominated organic species showed larger tropospheric mixing ratios in the tropics relative to mid-latitudes, which may reflect marine biogenic sources. Significant vertical gradients in the troposphere were observed for the short-lived species with upper troposphere values 40-70% of the lower troposphere values. Much smaller vertical gradients (3-14%) were observed for CH₃Br, and no significant vertical gradients were observed for the halons. Above the tropopause, the decrease in organic bromine compounds was found to have some seasonal and latitudinal differences. The combined losses of the individual compounds resulted in a loss of total organic bromine between the tropopause and 20 km of 38-40% in the tropics and 75-85% in mid-latitudes. The fractional dissociation of the halons and CH₃Br relative to CFC-11 showed latitudinal differences, with larger values in the tropics.

We were also able to quantify the amount and speciation of organic bromine compounds at the tropical tropopause. The amount of bromine entering the stratosphere from organic source gases is a primary factor involved in determining the magnitude of bromine catalyzed loss of ozone. Thirty-two whole air samples were collected at the tropical tropopause during the NASA STRAT Campaign in February, August, and December 1996 and were analyzed for brominated organic compounds. Total organic bromine was 17.4 ± 0.9 ppt with 55% from methyl bromide, 38% from the halons, 6% from dibromomethane, and 0.8% from bromochloromethane and dichlorobromomethane. One flight showed the presence of 0.42 ppt of additional organic bromine from bromoform and dibromochloromethane.

Methyl nitrate was measured for the first time in the lower stratosphere at altitudes to 20.5 km during the December 1996 NASA STRAT deployment. Methyl nitrate was found to have a mixing ratio ranging from 0.1 to 0.8 pptv, showing a maximum at subtropical northern latitudes. The observed behavior was reproduced by means of photochemical box model calculations, which showed that in the lower stratosphere, methyl nitrate is produced about equally from the reactions of CH₂O₂ with NO and CH₂O radicals with NO₂ with the latter reaction becoming more important with increasing altitude. From these model calculations, an estimate for the yield of methyl nitrate from the reaction of methyl peroxy radicals with NO was derived, leading to a branching ratio of $5-10 \times 10^{-5}$ for the lower stratosphere and $1.5-3 \times 10^{-4}$ for the lower troposphere.

Mixing ratio profiles of long-lived species in the tropical lower stratosphere were examined using a 1-D photochemical model that includes entrainment from the extra-tropical stratosphere and was constrained by measured concentrations of OH. Profiles of tracers found using the 1-D model agree well with all the observed tropical profiles for an entrainment time scale of 8.5 ± 5.3 months, independent of altitude between potential temperatures of 370 and 500 K. Tropical profiles of ethane and C₂Cl₄ reveal that the concentration of Cl is higher than expected based on photochemical model simulations using standard gas phase kinetics and established relationships

between total inorganic chlorine and CFC-11. Our observations suggest that short-lived organic chlorinated compounds and HCl carried across the tropical tropopause may provide an important source of inorganic chlorine to the tropical lower stratosphere.

With air samples from POLARIS and from an ad-hoc air archive from the Northern Hemisphere troposphere we examined halocarbon trends and stratospheric correlations. The vast majority of the halocarbon compounds reaching the stratosphere have anthropogenic sources and, therefore, have a temporal trend in the troposphere related to their industrial production, emission, and lifetime. The surface tropospheric trend in some halocarbons has been measured as part of long term monitoring efforts (CMDL, ALE/GAGE/AGAGE), and from selected archive samples. Tropospheric trends of halocarbons have been used to compare to reported emissions, to estimate lifetimes, and to evaluate atmospheric transport simulations. The historical trend of halocarbons in the troposphere also has been used to gain insight into stratospheric dynamics and "age of air." Trace gases with known tropospheric trend and negligible stratospheric loss rates have been used to estimate the mean age of the stratospheric air parcels.

Our results are based on measurements of long-lived perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), chlorofluorocarbons (CFCs) and hydrochlorofluorcarbons (HCFCs) obtained during the recent NASA POLARIS mission during May-September 1997. To better understand the relationships and correlations between tracers in the Arctic stratosphere, we also measured the same set of trace gases in a series of samples collected over the past two decades by Leroy Heidt and Walt Pollock of NCAR. The combination of temporal history of a number of long-lived gases was then compared to stratospheric data to provide a multi-tracer evaluation of stratospheric ages. The comparisons show: 1) As might be expected, the very long-lived perfluorocarbons, hexafluoroethane and octafluorocyclobutane, are potentially useful as tracers of air mass age. However, this is the first independent test of the use of anthropogenic halocarbons to measure age in the stratosphere. 2) More surprising, those trace gases which have shown sharp increases in the troposphere in the last 5-7 years appear to be well correlated between their temporal increase and their distribution in the stratosphere. These gases are HFC 134a, HFC 143a, HCFC 142b, and HCFC 141b. The rate of growth of these gases appears to exceed their chemical losses in the stratosphere; thus, a number of current and future HFCs and HCFCs may also be useful to examine transport processes in the lower stratosphere. 3) Fluoroform and CFC 115 show a close age correlation with SF₆. If trends derived here for these gases are accurate, the diagnostic use of fluoroform and CFC 115 may slightly overestimate stratospheric age. 4) Also as expected, other CFCs and halons do not correlate well between stratospheric observations and temporal history (though these correlations provide other useful diagnostic information, e.g., on relative lifetimes of trace gases).

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Measurement of Aerosol and Cloud Particles

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Research Objectives

The objective of this work was to employ an aerosol instrument, the Multiangle Aerosol Spectrometer Probe (MASP), on NASA sponsored high altitude payloads like the ER-2 and WB57F to measure aerosol and cloud particles. This includes collaboration with others in the various integrated studies which were undertaken.

Summary of Progress and Results

The MASP is an instrument which was designed and built under the auspices of the NASA High Speed Research Program and was flown for the first time on the ER-2 during the ASHOE/MAESA project. It counts and sizes particles in the nominal size range of 0.4 to 10 μm diameter and also provides estimates of the particle index of refraction over the size range of ~0.4 to 0.7 μm .

The MASP mounting location on the ER2 was changed to the exterior of the left superpod for the POLARIS mission. Measurements from the MASP instrument during the POLARIS mission from Alaska during 1997 demonstrate a low concentration background aerosol with insufficient surface area to have a significant effect on the ozone chemistry/photochemistry. However, on one flight (970513) particles of a very unusual shape and composition were detected with an increased surface area in a shallow layer at high latitude. These particles were detected in a layer too warm to be present as ice. The NASA-Ames wire impactor also obtained a sample in this layer and has confirmed the presence of unusual solid particles which remain stable even at room temperature and the reduced pressure of an electron microscope. These unusual particles are still a scientific puzzle and a draft paper describing them in more detail has been prepared. A presentation on these unusual particles was given at the Fall 1998 AGU meeting. Other presentations using the MASP data from this mission were made at the spring 98 AGU meeting in a SAGE session and also at the 1998 AEAP meeting in Virginia Beach by Tim Onasch from our group. The data from the POLARIS measurements is available from the public archive.

Theoretical work applying the T-matrix code of Mischenko on the scattering of light by spheroids to the MASP measurement system suggests that a parameter describing particle sphericity can be obtained from a combination of the MASP detector outputs. This is currently under evaluation by using past data and will be used to assist with SAGE satellite aerosol retrievals if the theory holds.

The MASP instrument was integrated to the WB57F right spear pod for the WB57F Aerosol Mission (WAM) in 1998. The WAM data will be used mostly for the upper tropospheric cirrus clouds which were observed. The data from this mission is currently being made ready for public distribution from an archive.

The MASP instrument was flown on all of the CiREX flights in late 1998. The MASP data was used to locate cirrus clouds and to provide cloud particle size distributions. A new instrument, Interferometer for Emission and Solar Absorption (INTENSA), from Harvard University which included channels relevant to cirrus cloud radiation fields was being tested during this mission.

The MASP instrument was integrated to the WB57F right spear pod for the WB57F Aerosol Mission (ACCENT) in 1999. The MASP data from this mission will be used to better understand the properties of the upper tropospheric cirrus clouds and the rocket plume particles which were observed during the mission. The MASP size distribution data from the rocket plume flights shows significant surface area above the normal background aerosol available for chemical reaction. These size distributions and the fast response time of the MASP will be used to understand the nitric acid measurements made by the NOAA Aeronomy Laboratory group during the rocket plume intercept on 990924. It is anticipated that 3 manuscripts using the MASP data from the ACCENT mission will be prepared and submitted for publication. The data from the ACCENT mission will be available from a public archive.

Preparations are underway for MASP participation in the SOLVE mission from Sweden in early 2000. The MASP will be used primarily for the detection of polar stratospheric clouds and ice clouds if the conditions are cold enough. The MASP mounting location will be moved from the left to the right super-pod for the mission to accommodate the SOLVE instrument payload.

A Ph.D. dissertation from the University of Colorado by Tim Onasch working with our group used MASP data from the POLARIS mission and also contributes to the laboratory work on refractive index measurement. A new Ph.D. student from the University of Colorado, Sarah Brooks, has recently joined our effort and will participate in the SOLVE campaign during 2000.

Publications

None

Stratospheric Chemistry and Transport Through Isotopic Analyses of Trace Gases

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Research Objectives

The isotopic composition of chemically and radiatively important stratospheric trace species, such as CO₂, CH₄, and N₂O, has remained largely unexplored, despite indications from the few measurements available that global-scale observations will provide a means of tracing chemical and transport processes in the stratosphere which is independent of, and complementary to, trace gas concentration measurements made from satellite-, aircraft-, and balloon-borne instrumentation. The objectives of this pilot study were to collect whole air samples from the ER-2 during the STRAT and POLARIS field missions in conjunction with simultaneous *in situ* measurements of numerous long-lived and short-lived species, archive the samples for subsequent analyses of the carbon, oxygen, and nitrogen isotope compositions of CO₂, N₂O, CH₄, and N₂, analyze a subset of the nearly 200 samples for δ¹⁷O and δ¹⁸O of CO₂, and demonstrate the feasibility and use of these new observations in studies of ozone and global change.

Summary of Progress and Results

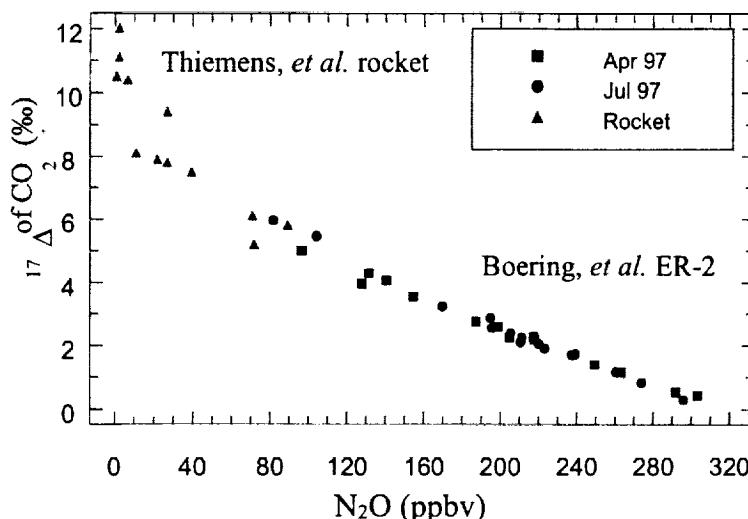
In 1996-1997, as part of the NASA STRAT and POLARIS field campaigns, 193 whole air samples were collected from the ER-2 aircraft from 2°S to 90°N over 4 deployments from December 1996 to September 1997 between 8 and 21.5 km. The deployments allowed for substantial sampling in the tropics and midlatitudes as well as in the Arctic vortex at the end of the winter of 1997, a year that showed record Arctic ozone losses. Simultaneous *in situ* measurements of CO₂ and SF₆ indicate that air which had descended from much higher altitudes (with mean ages as old as 6.5 years and N₂O values as low as 80 ppbv) was sampled. These samples therefore provide information on isotope fractionation occurring above the ER-2 ceiling, as anticipated. All samples have been transferred from the WAS canisters, appropriately treated,

and archived in glass flasks and ampoules. To date, 32 of the samples have been analyzed by KAB in the Thiemens laboratory for the oxygen isotopic composition of CO_2 , more than doubling the total number of observations available for the stratosphere. Analyses for CH_4 , N_2O , N_2 , and the remaining CO_2 samples will be carried out at UC Berkeley and at Princeton, supported in part by NSF.

Observations of Anomalous Fractionation in CO_2 : Results for the first 32 ER-2 samples run for oxygen in CO_2 provide new observation-based constraints on the source of the fractionation that leads to an unusual enrichment in both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (for which $\delta^{17}\text{O} \neq 0.52 * \delta^{18}\text{O}$), on the distribution of this anomalous (or “mass-independent”) fractionation in the stratosphere, and on its use as a tracer of stratospheric chemistry and transport. Laboratory experiments [e.g., Wen and Thiemens, 1993] and modeling studies [e.g., Yung *et al.*, 1997] suggest that the mass-independent fractionation in O_3 – due to an anomalous isotope effect in reaction (1) – is transferred to CO_2 via reaction with $\text{O}(\text{'D})$ produced from ozone photolysis:



The strong correlation of ${}^{17}\Delta$ in CO_2 (${}^{17}\Delta = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}$, *i.e.*, the degree of mass-independent fractionation) with N_2O from this work, combined with data from Thiemens *et al.* [1995], is consistent with such a mechanism (see figure). Like O_3 , ${}^{17}\Delta$ has a stratospheric source.



tropospheric source gases N_2O , CH_4 , and CO_2 , are losing theirs. These properties will be useful for studies of transport of air from the upper stratosphere to the lower stratosphere and may help resolve discrepancies between model predictions of mean age and mean ages determined from observations of gases with tropospheric sources [e.g., NASA Models and Measurements II Report, *in press*, 1999]. It may also serve as a tracer with production and transport terms proportional to those of ozone but with no chemical loss terms, thereby providing an index of integrated ozone production and transport and leaving integrated ozone loss as the free parameter to test against free radical observations and model results.

Like O_3 , ${}^{17}\Delta$ has a stratospheric source. However, unlike tracers with stratospheric sources that are now routinely measured from aircraft and satellites (such as O_3 or NO_y), this anomalous fractionation in CO_2 has no stratospheric sink. Its only loss mechanism is transport to the troposphere and subsequent isotope exchange with water in the biosphere and hydrosphere. Thus, the anomalous fractionation in CO_2 behaves as a long-lived tracer with a stratospheric source but no stratospheric sink. Moreover, it is picking up dynamic range in the upper stratosphere where the

The correlation of $^{17}\Delta$ of CO₂ with N₂O also provides a basis for estimating global-scale variations in the oxygen isotopic composition of stratospheric CO₂, given the extensive database of observations of N₂O from aircraft and satellites. Such estimates are proving valuable for studies of biogeochemical cycles in the troposphere. For example, because of the indirect isotope exchange in the stratosphere between O₂ and CO₂ (via reactions 1-3 above), stratospheric O₂ becomes anomalously depleted as stratospheric CO₂ becomes anomalously enriched. When air returns to the troposphere, anomalous CO₂ is destroyed on a time scale of about 1 year, as noted above. In contrast, the turnover time for O₂ in the atmosphere is about 1200 years and, therefore, the anomalous signature from the stratosphere can build up to detectable levels even though the production rate is small on an annual basis. Thus, the anomalous signature in O₂ represents a balance between photochemical production in the stratosphere and destruction by biosphere. With knowledge of the stratospheric processes, then, the anomalous isotopic composition of O₂ provides an index of modern primary productivity on Earth and, through ice core studies, changes in biological productivity on glacial-interglacial time scales. The new ER-2 measurements shown above have greatly informed preliminary work on these new ideas (see Luz *et al.* [1999] under Publications), and analyses of further ER-2 samples will provide the basis for more systematic studies of the interactions between the stratosphere and biosphere in the future.

Future Work: Analysis of the remaining samples for CO₂ and all the samples for N₂O, CH₄, and N₂ will extend the existing stratospheric isotopic database by an order of magnitude and will provide the first isotope observations to be obtained in conjunction with simultaneous *in situ* measurements of numerous long-lived and short-lived chemical species and meteorological parameters. The observations will be interpreted using a combination of empirical tracer correlations and 2D and 3D model results (with modeling support from NASA ACMAP) with a view towards (a) establishing a database of the global-scale variations in stratospheric isotope compositions, (b) quantifying vertical and horizontal transport in different regions of the stratosphere (including horizontal exchange between the high and middle latitudes in summer and between the tropics and extratropics in the northern winter and autumn seasons), (c) distinguishing chemical ozone loss over the polar summer from ozone changes due to transport alone, (d) improving estimates of rates for stratosphere-troposphere exchange, and (e) deriving estimates from observations of the influence of stratospheric fractionation processes on the isotopic compositions of tropospheric CH₄, N₂O, CO₂, and, by inference, O₂.

Publications

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Measurements of Particle Size Distributions in the 4 to 2000 nm Diameter Range in the DC-8 for the SAGE III Ozone Loss Validation Experiment (SOLVE)

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Research Objectives

The research objective is to prepare an aerosol measurement package for the DC-8 for use in the SAGE III Ozone Loss Validation Experiment (SOLVE). SOLVE is scheduled to occur from December 1999 through March 2000. The aerosol package being prepared for SOLVE will permit measurement of aerosol size distributions in the diameter range from 4 to 2000 nm. Polar stratospheric clouds (PSCs) will not be measured by these instruments since they heat the particles prior to measurement. However, the sulfate aerosol that serves as nuclei for the PSCs will be measured. The size distributions will permit calculations of extinction for comparisons with satellite measurements and will permit calculation of aerosol surface to permit studies of non-PSC heterogeneous chemistry. The instruments to be used include the Nuclei Mode Aerosol Size Spectrometer (NMASS), the Focused Cavity Aerosol Spectrometer II (FCAS), and a shrouded, passive, isokinetic aerosol inlet.

Summary of Results and Progress

The instrument mountings and inlet have been designed and are being fabricated. The integration on the DC-8 is proceeding on schedule. This project started in February 1999 and hardware is being developed on schedule but no scientific results are expected until after SOLVE.

Publications

None

Airborne Lidar Stratospheric Ozone, Water Vapor, and Aerosol Investigations

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Research Objectives

An airborne lidar is used to remotely measure the distribution of ozone (O_3) and aerosols in the lower stratosphere, and these observations are related to chemical and dynamical processes that can contribute to changes in stratospheric O_3 , including those possibly associated with aircraft emissions. Observations of O_3 distributions are important in the direct detection of the spatial and temporal variations of O_3 changes, and the distribution and characteristics of stratospheric aerosols and polar stratospheric clouds (PSCs) are required to understand heterogeneous chemical processes that can lead to O_3 depletion. Both O_3 and aerosols can also be used as tracers of transport in the lower stratosphere and between the stratosphere and troposphere. To obtain remote measurements of O_3 and aerosols/PSCs in the lower stratosphere, an airborne Differential Absorption Lidar (DIAL) system is operated in a zenith mode from the NASA DC-8 aircraft on long-range flights from the polar regions to the tropics. The observed variability of O_3 and aerosols is related to the atmospheric processes that can contribute to O_3 changes. A second DIAL system, the Lidar Atmospheric Sensing Experiment (LASE), was recently added for measurements of water vapor.

Summary of Progress and Results

We have continued to investigate various transport processes in the lower stratosphere using the airborne DIAL O_3 and aerosol data obtained during the 1995/1996 Tropical Ozone Transport Experiment/Vortex Ozone Transport Experiment (TOTE/VOTE). Ozone data from the UV DIAL system were compared with ground-based DIAL systems and several space-based ozone instruments, finding very good agreement with all instruments, except in a few altitude regions, where the various instruments have known problems. The aerosol and O_3 data from the airborne lidar provided the detailed spatial information needed to determine the structure and transport of the air in the lower stratosphere from the polar regions to the tropics. In collaboration with a scientist in Norway, it is being shown that laminar transport from the polar regions to the tropical stratospheric reservoir occurred during the TOTE/VOTE mission days, in agreement with the UV DIAL observations. The European Center for Medium-range Weather Forecasting (ECMWF) data base is being used for the transport calculations. Two manuscripts on this research are being prepared for submission for publication.

The UV DIAL system participated in the NASA Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SONEX) mission in October and November 1997. The objectives of the mission included characterizing the upper troposphere/lower stratosphere over the Atlantic flight corridor and looking for evidence of aircraft emissions or effects on this region of the atmosphere. The UV DIAL system measured ozone and aerosols from the surface to 4 km above the tropopause. Many stratospheric intrusions were observed during this mission, and comparisons were made with modified potential vorticity fields calculated by the Goddard Space Flight Center, showing very good to excellent agreement. One manuscript has been submitted based on data obtained during this mission. It discusses stratospheric intrusions associated with transport of marine boundary layer and lower troposphere air transported from the tropics to mid-latitudes.

Preparations are being made to use both the UV DIAL and the LASE systems during the NASA SOLVE (SAGE III Ozone Loss and Validation Experiment) field campaign. Both will be operated from the DC-8 aircraft. The UV DIAL will provide high-resolution profiles of ozone and aerosols in the lower-to-mid stratosphere. LASE will provide high-resolution profiles of water vapor, aerosols, and clouds throughout the troposphere and into the lower stratosphere. These measurements will be used to characterize the Arctic troposphere and lower stratosphere in order to understand and model the mechanisms responsible for ozone loss during the Arctic winter. Simultaneous ozone, water vapor and aerosol profiles measured by the UV DIAL and LASE along the DC-8 flight tracks will be used to map features associated with atmospheric dynamics and to study transport in the upper troposphere and lower stratosphere in the high latitude Arctic region, including regions of the polar vortex. The LASE aerosol measurements at 815 nm will be used to help identify chemical and physical characteristics of the Polar Stratospheric Clouds (PSCs) needed to study ozone loss mechanisms. The UV DIAL and LASE preparations for SOLVE have included testing and upgrading optical and electronic components associated with the laser subsystems, and modeling the expected atmospheric return signals.

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DC-8 Measurements of ClO, BrO, and HO_x During SOLVE

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Research Objectives

Current models underpredict the ozone loss trend in the lowermost stratosphere at high latitudes. Accounting for this ozone loss is particularly difficult in the lowermost stratosphere, a region between 8-12 km that is influenced by both stratospheric and tropospheric air and by heterogeneous chemistry. SOLVE (SAGE III Ozone Loss and Validation Experiment) is designed to address ozone loss in the lowermost stratosphere and upper troposphere by including measurements of hydroxyl (OH), hydroperoxyl (HO₂), chlorine monoxide (ClO), bromine monoxide (BrO), and nitric oxide (NO) from the NASA DC-8 aircraft. SOLVE takes place from Kiruna, Sweden in the winter of 1999-2000. This research effort is an attempt to examine the catalytic ozone destruction budget in the lowermost stratosphere by measuring for the first time at these altitudes all the key rate-limiting species: ClO, BrO, NO₂ (by NO), and HO₂. We will also be able to test key heterogeneous halogen processes that involve both halogen and hydrogen species. These measurements will complement the ER-2 based measurements from above ~15 km and will extend the study of ozone catalytic destruction by ClO, BrO, HO_x into virtually unexplored regions between 12 km and the tropopause near 8 km. In addition, measurements will also be made in the cloud-filled upper troposphere to look for evidence of the tropospheric BrO that is indicated by recent GOME (Global Ozone Monitoring Experiment) measurements.

Summary of Progress and Results

Because SOLVE is yet to occur, we have no scientific results to report. However, we made significant progress in preparing the instrumentation for measuring the free radicals OH, HO₂, ClO, and BrO in the lowermost stratosphere and upper troposphere from the NASA DC-8 aircraft. The instrumentation is a combination of instruments, one that measures OH and HO₂, developed by our group at the Pennsylvania State University, and one that measures ClO and BrO, developed by Toohey and coworkers, now at the University of Colorado. The progress on developing the combined instrument will be discussed in this summary, but the specifics of the ClO/BrO instrument will be contained in a separate report by Toohey, since the grants for the two groups are distinct.

The OH and HO₂ measurements will be made with ATHOS (Airborne Tropospheric Hydrogen Oxides Sensor), which was developed initially to study the influence of subsonic aircraft on the chemistry of the upper troposphere. In this technique, air is drawn through a small inlet by a

vacuum pump and pulled at low pressure through detection axes, where OH and HO₂ are detected simultaneously by laser induced fluorescence (LIF). HO₂ detection requires the addition of reagent nitric oxide (NO), which converts HO₂ to OH, which can then be detected by LIF. Based on previous missions, we anticipate that the OH and HO₂ detection limits will be less than 0.015 pptv in about a minute (S/N = 2).

ClO and BrO are measured by resonance fluorescence using emission lines from trace amounts of chlorine and from bromine in radio-frequency-excited helium plasma lamps, following chemical conversion of ClO to Cl and BrO to Br by the addition of reagent NO. This detection technique has greater sensitivity if the measurements are made in air at pressures near 10 hPa. This low pressure and the use of the NO reagent suggest that ClO/BrO can be detected using the ATHOS sampling system simply by inserting ClO and BrO detection axes behind the OH detection axes in ATHOS. In this way, OH, HO₂, ClO, and BrO can efficiently be detected together by the combination of instruments.

Our approach is to add the ClO and BrO detection axes to ATHOS, but to keep the electronics and data collection separate. Including the ClO/BrO detection axes requires that we use only one OH detection axis and sequentially add NO to measure alternately OH and then HO₂, and consequently, ClO and BrO. The main mechanical modifications necessary to combine the two instruments have been completed. Preliminary fit-checks show that no significant issues remain. The integration of the two instruments is scheduled to occur in late September 1999. We anticipate having to resolve small problems and to optimize sampling strategies, but this work will occur during the course of integration onto the NASA DC-8, which begins in late October 1999.

Publications

None

The ER-2 Meteorological Measurement System (MMS)

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Research Objectives

The objectives are to instrument the NASA ER-2 high-altitude aircraft to measure accurate, high resolution, and fast-response *in situ* meteorological variables (temperature, pressure and winds), to participate in field studies, and to interpret the resulting data to advance our understanding of the lower stratosphere.

Summary of Progress and Results

The MMS successfully completed the Photochemistry of Ozone Loss in the Arctic Region in the Summer (POLARIS) in Fairbanks, Alaska and at Barbers Point, Hawaii. Preliminary data were distributed during the mission for in-field analysis. Final calibrated data were generated during post-mission for archival. The data processing included several refinements to improve data quality. An upwash correction to the angle-of-attack measurements was incorporated as a function of fuel-load. The vertical aircraft velocity is more accurately computed using a hydrostatic altitude feedback in the numerical integration. The hydrostatic altitude, derived from the integration of the hydrostatic equation and included temperature gradient information, significantly improved the vertical wind computational during altitude profiling.

For the coming SAGE-III Ozone Loss and Validation Experiment (SOLVE), the following modifications are planned: (1) installation of the dedicated pitot/static system which is independent of the aircraft avionics; (2) improvement of the pressure measurements with temperature compensated sensors; (3) improvement of position data to meter/sub-meter accuracy with differential GPS data; and (4) upgrade the data acquisition system for performance while reducing weight.

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Airborne Raman Lidar

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Research Objectives

NASA's Goddard Space Flight Center and Langley Research Center, working together, have developed a lidar for installation onboard NASA's DC-8 aircraft. This instrument is designed to measure tropospheric and stratospheric aerosols, polar stratospheric clouds, ozone and temperature from flight altitude (12 km) to an altitude of ~50 km in support of detailed studies into atmospheric chemistry. During the upcoming SOLVE (Sage Ozone Loss and Validation Experiment) mission (1999-2000 winter) these measurements will provide a detailed snapshot of the processes responsible for controlling polar to mid-latitude stratospheric ozone levels. Besides chemistry this instrument will play a major role in providing the correlative measurements necessary to validate the data products (aerosols, ozone and temperature) of the SAGE III (Stratospheric Aerosol & Gas Experiment) instrument after launch next year.

Summary of Progress and Results

The Airborne Raman Lidar is a modification of the Methane Lidar that was developed for deployment on the NASA DC-8 during the TOTE/VOTE campaign in 1995/1996. The instrument has been modified to measure vertical profiles of ozone and aerosols, along with the temperature measurement from the previous instrument. Two different lasers are used in the transmitter: a Nd-YAG laser transmitting at 1064, 532, and 355 nm, and a XeCl laser

transmitting at 308 nm. The receiver has been extensively modified to be significantly smaller than previously. Four wavelengths are transmitted, and six wavelengths are received. In addition to detecting all the transmitted wavelengths, Raman scattered radiation from the two transmitted UV wavelengths is received. The Raman scattered wavelengths are at 332 and 387 nm.

Ozone is extracted from the UV wavelengths using the DIAL and Raman DIAL techniques used in the GSFC NDSC Stratospheric Ozone Lidar. The Raman returns are used in areas of aerosol loading to minimize the effects of aerosol backscattered radiation. Temperature is extracted from the 332, 355, and 387 nm radiation. In both cases these parameters are expected to be measured down to the skin of the aircraft. Ozone profiles from the skin to above 40 km should be recovered in 2.5 to 5 minutes of integration and will have a vertical resolution between 0.5 and 4 km. This varies as a function of distance from the aircraft. Temperature will be retrieved in the same time frame from the skin of the aircraft to over 50 km with roughly the same resolution as the ozone measurement. As with the ozone measurement, the Raman returns are used to minimize the effects of aerosols on the temperature retrieval.

Aerosol and cloud measurements will be made with the 532- and 1064-nm wavelength channels. Aerosol measurements will provide information on the background stratospheric aerosol loading and identify the edge of the polar vortex. Cloud measurements will focus on determining the presence and phase of polar stratospheric clouds (PSCs) which are a catalyst to ozone destruction in the stratosphere. Cloud and aerosol profiles will have a 40 meter vertical resolution with ~1 km footprint.

The detector assembly was reconfigured to allow a total of twenty data channels instead of the previous six; this was accomplished using a new, much smaller, photon counting photomultiplier, special PMT gating circuits, a mechanical chopper and membrane mirror. Additional enhancements provide aerosol extinction and depolarization information that permits the unambiguous detection of polar stratospheric clouds and provides a correction to the temperature calculation allowing temperature retrievals within polar stratospheric clouds.

Publications

None

Airborne, Infrared Fourier Transform Spectroscopy

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Research Objectives

The objectives of this work are to use infrared spectroscopy to study the chemical and physical processes which control ozone in the stratosphere and upper troposphere. Using high resolution Fourier transform spectrometers, based on aircraft platforms (and on the ground), we obtain column amounts for ozone and a number of trace gases important to its chemistry, including NO, NO₂, HNO₃, HCl, HF, ClONO₂. Infrared spectra also will be used, during the SAGE III Ozone Loss and Validation Experiment (SOLVE), to attempt to define the composition and character of polar stratospheric clouds.

Summary of Progress and Results

Using observations from previous airborne, polar, winter-time missions we have analyzed our data to produce vortex-wide distributions of important stratospheric gases. We describe an integrated view of polar stratospheric chemistry based on our column observations of HCl, HF, NO, NO₂, HNO₃, ClONO₂ and O₃. Column amounts are related to the potential vorticity at a given level and relationships established which allow vortex wide distributions to be calculated for nitrogen and chlorine families and individual chemical constituents.

Ground-based observations at Sondre Stromfjord, Greenland have been used in two studies of stratospheric chemistry and dynamics.

Substantial modifications have been made to our airborne spectrometer to make it better able to observe the spectrally broad and very low intensity infrared signature of polar stratospheric aerosols. Infrared spectral measurements from aircraft have the potential to provide the phase and composition of PSCs. Our spectrometer will be part of the NASA DC-8 payload for SOLVE.

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Airborne Trace Gas Measurements

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Research Objectives

ACATS-IV is a four-channel gas chromatograph that operates in the Q-bay of the NASA ER-2 aircraft. The instrument is currently configured with four electron-capture detectors to measure CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 ($\text{CCl}_2\text{FCClF}_2$), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), halon-1211 (CBrClF_2), chloroform (CHCl_3), methane (CH_4), and hydrogen (H_2) every 125 seconds, and nitrous oxide (N_2O) and sulfur hexafluoride (SF_6) every 250 seconds. This sampling rate of ACATS-IV will be improved during the SAGE-3 Ozone Loss Validation Experiment (SOLVE). Measurements from ACATS-IV permit the calculation of the mean age of the air mass, inorganic and organic chlorine, and inorganic and organic bromine. ACATS-IV participated in the Photochemistry of Ozone Loss in Arctic Region in Summer (POLARIS) mission in 1997 and the Tracer Intercomparison Experiment for SOLVE (TIES) intercomparison, primarily for N_2O measurements, in September 1999. The main research objectives of our work are (1) to measure these trace gases as accurately as possible; (2) determine the hydrogen budget, including CH_4 , H_2 , and H_2O , in the stratosphere; (3) study stratospheric transport; (4) calculate the mean age of the air mass; (5) ascertain the stratospheric lifetimes of the trace gases; and (6) determine the bromine and chlorine budgets of the stratosphere.

Summary of Progress and Results

Calibration and Validation (cal-val) of Trace Gases: ACATS-IV provides accurate measurements of 11 trace gases because of its frequent calibration (once every 4 injections). Both ambient air and standard gas are injected at the same pressure and temperature to minimize systematic analysis errors (see Elkins *et al.*, *Geophys. Res. Lett.*, 23 (4), 347-350, 1996). ACATS-IV measurements have been used to "cal-val" trace gas measurements by space-borne and airborne instruments, including the Atmospheric Trace MOlecule Spectroscopy (ATMOS) instrument on NASA's Space Shuttle (see Chang *et al.*, 1996, *Geophys. Res. Lett.*, 23 (7), 2389-2396); MkIV balloon Fourier Transform-InfraRed (FT-IR) spectrometer [Toon *et al.*, 1999]; DC-

8 instruments [Weinheimer *et al.*, 1998] and Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) satellite [Bacmeister *et al.*, 1999].

Bromine and Chlorine Budgets: ACATS-IV measures about 80% of total organic chlorine in the stratosphere. The unmeasured species, primarily CH₃Cl and HCFC-22, can be estimated by tracer-tracer correlations derived from flask samples taken by the Whole Air Samplers (WAS). Total Chlorine for each altitude can be calculated as the mixing ratio of the all source gases at the time of entry into the stratosphere. Precise estimate of Total Chlorine can be recovered from the recorded tropospheric trends of the source gases and the mean age of the air mass calculated from measurements of either SF₆ or CO₂ (see Woodbridge *et al.* [1995], *J. Geophys. Res.*, 100 (D2), 3057-3064). Inorganic chlorine is just the difference between Total Chlorine and organic chlorine. The agreement between organic and inorganic chlorine values calculated from ACATS-IV and WAS data is within the experimental error of both instruments. A similar approach for calculating organic and inorganic bromine in the stratosphere [Wamsley *et al.*, 1998] was undertaken using ACATS-IV halon-1211 measurements which represent about 15% of the total organic bromine entering the stratosphere. Total inorganic bromine calculated from BrO measurements and from our analysis were different, yet the discrepancy was within the experimental errors of the two techniques. The large difference (30%) indicates that there may be a missing contributor of organic bromine (e.g., bromoform (CHBr₃)) or an inorganic compound passing across the tropopause, or a potential problem with the calibration of BrO.

Tropical Stratospheric Transport: There exists a partial barrier to transport between the stratospheric extratropics and tropics. The rate of entrainment and the fraction of midlatitude air entrained in the tropics were estimated from measurements by ACATS-IV and other instruments on the NASA ER-2 aircraft [Volk *et al.*, 1996] (*Science*, 272, 1763-1768). For example, about 50% of air at 20 km in the tropics is of mid-latitude origin.

Stratospheric Lifetimes: Tracer-tracer and tracer-age correlations permit the determination of stratospheric lifetimes for a number of trace gases. Using both correlations, Volk *et al.* [1997] recommended shorter lifetimes for halon-1211, CFC-11, and CCl₄ which were later accepted in the *WMO Scientific Assessment of Stratospheric Ozone Depletion: 1998*.

Closure of the Hydrogen Budget: Based on measurements of H₂, CH₄, and H₂O, the hydrogen budget of the stratosphere is consistent with current chemical understanding. No significant trend was observed in ER-2 aircraft data for H₂O + 2*CH₄ in the lower stratosphere from 1993 through 1997 [Hurst *et al.*, 1999].

Mean Age of the Air Mass: Compared to mean age of air masses calculated from SF₆ and CO₂ measurements, general circulation models tend to underpredict mean age by as much as a factor of 2 (see Hall *et al.* [1999], *J. Geophys. Res.*, 104 (D15), 18815-18839, 1999). Model transport uncertainties greatly affect the accuracy of estimated environmental impacts of long-lived trace gases in the stratosphere.

Future Plans: We plan to implement rapid gas chromatography techniques on two channels that will permit measurements of CFC-12, halon-1211, N₂O, and SF₆ every 70 seconds.

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Reactive Nitrogen Measurements on the ER-2 High Altitude Aircraft

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Research Objectives

A multi-channel instrument for the measurement of reactive nitrogen species has been operated on board the NASA ER-2 high altitude aircraft. The instrument provides *in situ* measurements of NO, NO₂, and NO_y each second of flight path using a combination of techniques that include catalysis, photolysis and NO/O₃ chemiluminescence. Each instrument channel is calibrated in flight. For each flight, mixing ratios of measured species along the flight track are calculated and submitted to a data archive for the planning of subsequent flights and for later interpretation.

Summary of Progress and Results

The reactive nitrogen instrument participated in the 1997 Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) mission. The mission included flights from Alaska, California, and Hawaii in the spring, summer, and fall seasons. Data for NO, NO₂, and NO_y were archived for nearly all flights in this mission. In 1999, preparations were begun for the instrument to participate in the SAGE III Ozone Loss and Validation Experiment (SOLVE) to be conducted in the northern winter of 1999/2000.

Publications

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Diode Laser Airborne Water Vapor Measurements

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Research Objectives

The Diode Laser Spectroscopy task consists of two primary efforts: development and deployment of near-infrared ($1 - 2.1 \mu\text{m}$) tunable diode laser (TDL) spectrometers for *in situ* gas sensing, and the laboratory acquisition and analysis of molecular spectral parameters required for interpretation of diode laser field spectra. Development of improved algorithms for data processing and autonomous spectrometer operation is also an important component of the research program. Two laser hygrometers were designed and built under this task during FY96-98, and upgraded during FY99 for measurements of atmospheric water vapor from the NASA DC-8 and ER-2 aircraft. These instruments use high-resolution absorption spectroscopy over fixed paths with a TE-cooled near-infrared TDL at $1.37 \mu\text{m}$ wavelength. They will participate in the FY2000 SOLVE mission out of Sweden.

Summary of Progress and Results

Following successful flights of the JPL laser hygrometer on the NASA ER-2 aircraft during the 1997 POLARIS mission, a second instrument was designed and built for the NASA DC-8. This instrument participated in the third Convection and Moisture Experiment (CAMEX-3) out of Patrick AFB in Florida during August-September 1998. Intercomparisons with two chilled mirror hygrometers aboard the DC-8, as well as the JPL surface acoustic wave (SAW) hygrometer, indicate that the TDL measurements are superior both in absolute accuracy and precision on a flight-to-flight basis. In addition, because of the external, open-path configuration, the TDL hygrometer was not subject to false readings, or "overshoot," due to vaporization of condensed phases of water (i.e., liquid or ice) at the sampling inlet in cloud encounters. This overshoot problem is common with hygrometers utilizing a sampling probe to bring air into the detection region, and prevents accurate vapor phase measurements in clouds. Data analysis for the CAMEX-3 flights has been completed and several collaborations are underway with groups at NASA Ames, NCAR, and JPL. Laboratory spectroscopic measurements in support of the ALIAS and ALIAS II instruments are also an ongoing component of the laboratory spectroscopy task.

The bulk of FY99 has been occupied with analysis of data from the POLARIS and CAMEX-3 missions, writing the TDL components of chapters 1 and 2 of an upcoming SPARC book detailing atmospheric water vapor measurements and instrumentation, and designing a new calibration system for the near-IR laser hygrometers. The remainder of FY99 and early FY2000 has been dedicated to completing the laboratory calibration facility, preparing the laser hygrometers for the upcoming SOLVE mission, and upgrading the ER-2 instrument. The electronics and software upgrades will incorporate the higher-speed laser control and signal processing circuitry developed for the DC-8 instrument, which should improve in-flight signal-to-noise ratios by minimizing the influence of beam jitter at the detector caused by high-speed air flow between the Herriott cell mirrors. The new calibration system incorporates a Licor dew point generator, precision MKS flow controllers for dilution, and a General Eastern chilled mirror hygrometer for verification of the generated dew points. This system allows automated and routine calibration of both instrument, simultaneously, and should result in absolute accuracies in the 2% range for SOLVE (depending on altitude and in-flight signal-to-noise ratios).

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Research Objectives

The Ames Earth Science Project Office (ESPO) managed two major field campaigns during this reporting period focused on stratospheric chemistry and dynamics. These missions were sponsored by the Upper Atmosphere Research Program (UARP), the Atmospheric Chemistry Modeling and Analysis Program (ACMAP), and the Atmospheric Effects of Aviation Project (AEAP). We also managed a major field campaign to study tropospheric chemistry, which was supported by the Subsonic Assessment Project under AEAP. The Stratospheric Tracers of Atmospheric Transport (STRAT) was a multi-year experiment, which was completed in December 1996. STRAT used the ER-2 aircraft and high altitude balloons to understand the nature of global-scale transport of long-lived chemical tracers. The goal was to determine the likely transport and distribution of exhaust emissions from a future fleet of high-speed civil transports (HSCTs). The Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) was conducted from Fairbanks, Alaska in 1997. Its primary scientific objective was to understand the behavior of polar stratospheric ozone as it progressed through the cycle of high concentrations in the springtime to the very low concentrations in the autumn. The Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SONEX) was conducted in the North Atlantic flight corridor in 1997. The goal of SONEX was to better understand and assess the impact of the subsonic fleet of commercial aircraft on the chemistry of the troposphere.

Summary of Progress and Results

The role of the Earth Science Project Office is to provide overall management of the airborne field campaigns sponsored by UARP, ACMAP and AEAP. The project management role entails the coordination among the Headquarters Program Management, Project Scientists, Science Investigators, Aircraft Operations and the host organizations. Based on the scientific objectives, we help define the mission requirements for instrumentation, flight hours and field logistics. From the requirements we develop and implement an overall mission plan. We also manage the exchange and archiving of the datasets from the experiments and we provide meteorological support by fielding a meteorological satellite downlink and display system. The datasets from the experiments are published and distributed on CDROM.

The STRAT mission was successfully completed in December 1996. It was conducted using the NASA ER-2 aircraft, instrumented for *in situ* chemistry measurements, to make flights from NASA Ames Research Center in northern California and from Barber's Point in Hawaii. It was coordinated with the Observations from the Middle Stratosphere (OMS) balloon campaign which made high altitude balloon profiles from Fort Sumner, New Mexico, Lynn Lake in Canada, and Juazeiro do Norte in Brazil. The data from these two experiments were published on CDROM in November 1997.

POLARIS was successfully conducted over three separate intensive field phases in 1997. The campaign primarily utilized the NASA ER-2 and balloon platforms based in Fairbanks, Alaska to make measurements of select species within the reactive nitrogen (NO_y), halogen (Cl_y), and hydrogen (HO_x) families; aerosols; and other long-lived species in the lower and middle stratosphere. The POLARIS campaign included a total of 30 ER-2 flights and 3 balloon flights in 3 deployment periods in 1997: 17 April to 15 May, 24 June to 13 July, and 3 to 27 September. The data from POLARIS were published on CDROM in July 1998.

SONEX employed the NASA DC-8 aircraft to make chemical and dynamical measurements in the North Atlantic flight corridor in the fall of 1997. The primary scientific objective was to understand the impact of subsonic aircraft exhaust on the tropospheric nitrogen oxide (NO_x) and ozone budgets. The mission was coordinated with a European field campaign (POLINAT) which used the German (DLR) Falcon aircraft to make similar chemical measurements. The experiment was conducted from Bangor, Maine and Shannon, Ireland with a stop in the Azores which allowed a complete transect of the northern Atlantic. The data from SONEX were published on CDROM in September 1998.

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Stratospheric N₂O Tracer Studies with the ATLAS ER-2 Diode Laser Spectrometer

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Summary of Progress and Results

During the past several years we have participated in a number of focused stratospheric research studies with the ATLAS (Airborne tunable laser absorption spectrometer) tracer measuring instrument on the ER-2 aircraft. ATLAS is a diode laser spectrometer used for *in situ* quantitative detection of N₂O, a chemically very stable molecule which thus acts as a tracer of stratospheric motions. This instrument has been actively deployed in stratospheric research since 1987 in a variety of Upper Atmosphere Research Program missions.

STRAT Experiment: The goal of STRAT (Stratospheric Tracers of Atmospheric Transport) is the measurement of the distribution of long-lived stratospheric tracers and dynamical quantities as functions of altitude, latitude and season. The guiding goal of the research is to determine rates for global-scale transport and future distributions of high speed civil transport (HSCT) exhaust emitted into the lower stratosphere. Of special interest in the STRAT experiment is the region near the tropopause, especially in the tropics where transport both into and out of the stratosphere of important trace chemicals is expected to occur. Horizontal transport rates within the lowermost stratosphere are also a focus of interest.

Joint studies of H₂O and N₂O in the lower stratosphere during STRAT have led to some increased understanding of transport that couples the upper tropical troposphere and the lowermost stratosphere [Hintsa *et al.*, 1998].

POLARIS Experiment: Throughout the POLARIS (Photochemistry of Ozone Loss in the Arctic Region in Summer) campaign carried out from a base in Fairbanks, Alaska in 1997, ATLAS provided accurate and reliable N₂O tracer field measurements on the ER-2 platform. These data were widely used by other POLARIS experimenters to provide a stable altitude dimension to aid in interpretation of the important chemical species involved in the ozone chemistry [POLARIS, 1999].

CiREX/TIES Experiments: Two recent campaigns on the ER-2 provided an ideal opportunity to intercompare different N₂O measuring instruments. The Cirrus Radiation Experiment (CiREX) test flights in 1998 provided a flight opportunity to intercompare 2 Ames tracer instruments: ATLAS and the newer dual channel Argus instrument previously deployed only on balloon platforms. Results are briefly reported in Jost *et al.* [1999]. A second campaign in late 1999,

TIES, intercompared ATLAS, Argus, a whole air sampler, a gas chromatograph and another diode laser spectrometer, ALIAS all measuring N₂O. Results from this campaign are still under study.

Global N₂O Morphology: Based upon 10 years of stratospheric N₂O measurements with ATLAS at many different latitudes, Dr. Susan Strahan of NASA Goddard produced representative curtain maps of N₂O for 4 seasons. This analysis has been published [Strahan *et al.*, 1999] and is expected to be of great value to modelers seeking to incorporate accurate dynamics into global chemical models of the stratosphere.

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Microwave Temperature Profiler (MTP)

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Research Objectives

The primary objective of this program is to make passive, remote temperature measurements above and below the flight altitude of atmospheric research aircraft, and thereby provide meteorological context for *in situ* and remote measurements of atmospheric gases and aerosols. In addition, these measurements are used to provide molecular number density profiles along the flight track (for more accurate mixing ratio determinations), and to study meso- to synoptic-scale wave phenomena in the atmosphere. The real-time display of Microwave Temperature Profiler (MTP) measurements has also been used to achieve particular research goals, such as flying at specific altitudes with respect to the tropopause, or flying isentropically.

Summary of Progress and Results

From 1997 to 1999 the MTP was used to support six field deployments aboard the NASA ER-2, DC-8, and WB-57F research aircraft. These included:

- POLARIS (Photochemistry of Ozone Loss in the Arctic Region in Summer), April-May 1997, June-July 1997, September 1997, ER-2.
- WAM (WB-57F Aerosol Mission), March-April 1998, WB-57F.
- SONEX (Subsonic Assessment, Ozone and Nitrogen Oxide Experiment), October-November 1997, DC-8.
- CiREX (Cirrus Radiation Exchange experiment), October-November 1998, ER-2.
- PEM Tropics B (Pacific Exploratory Mission in the Tropics B), January-April 1999, DC-8.
- ACCENT (Atmospheric Chemistry of Combustion Emissions Near the Tropopause), March-April 1999, August-September 1999, WB-57F.

During POLARIS the MTP obtained temperature profiles on all science and ferry flights. MTP's principal role was to establish tropopause altitudes during staircase flights to support tracer studies. An analysis of isentrope "wrinkle" amplitude showed that the Arctic summer has

isentrope surfaces that are smoother than for any previous ER-2 mission. Regional and seasonal correlations are now becoming well established, and are consistent with the Upper Atmosphere Research Satellite (UARS) Microwave Limb Sounder (MLS) findings, which are for longer spatial scales than measured by the MTP.

On WAM the ER-2 MTP was augmented with a real time analysis computer and modified DC-8 graphics software to provide an altitude temperature profile (ATP) display in the back seat of the WB-57F aircraft. This worked very well when it was used during two of the six WAM flights to fly at the tropopause for science reasons. Another highlight of the WAM flights was an encounter on April 11, 1998 with a predicted arctic vortex filament over Montana. Severe clear air turbulence (CAT) was encountered at 18 km, and MTP-measured temperature inversions as large as 10 K were seen.

During SONEX MTP performed its normal role of providing meteorological context for *in situ* measurements. A significant enhancement in MTP usefulness was also introduced on the last several SONEX flights, where — for the first time — MTP-derived color-coded temperature curtains (CTCs) were displayed in real time. This now makes it much easier to follow trends in parameters such as the tropopause altitude.

The CiREX mission was flown on the ER-2 in collaboration with the Anderson Group from Harvard University. The MTP performed well during all flights, and calibrated data for the CiREX flights has been provided to the Anderson Group.

During the April 1999 ACCENT test flights, a new MTP sensor unit was flown for the first time, and performed very well. The science flights will occur in September 1999.

During PEM Tropics B, a MTP flew on the DC-8 for the first time in the tropics. Its primary function was expected to be that providing number density profiles to remote sensing instruments. In fact, the number density profiles did not vary much from standard atmospheric models with monthly stratification. We believe that the most useful role of the MTP was to “see” the influence of mid-latitude air in the tropics, and that this might not have otherwise been recognized. MTP was also important for identifying cloud top inversions, stalactites, stratospheric intrusions, and tropopause folds.

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Composition and Photodissociative Flux Measurements

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Research Objectives

The Composition and Photodissociative Flux Measurement (CPFM) experiment provides quantitative information about the photodissociation rates of a number of chemical reactions in the stratosphere and provides essential diagnostic information about the radiation field present at stratospheric flight altitudes. The experiment also provides direct measurements of the column amount of ozone above the aircraft with a precision and accuracy unattainable by other means, such as estimating the amount from the TOMS satellite data in the vicinity of the aircraft location. The albedo (reflectivity) of the surface below the aircraft is also directly measured. 'Fish-eye', digital photographs of the field of view below the aircraft are collected using a video imager mounted in the instrument pod so that cloud pattern and surface reflectivity variability can be assessed.

These measurements are used for the evaluation of the performance of models used to calculate the photodissociation rates for significant reactions in the stratosphere, to assess the role of clouds in controlling the rates of photodissociation in the stratosphere and as input to photochemical model simulations of the chemical data collected. The CPFM team also operates a Brewer Ozone Spectrophotometer at the aircraft operational base to make accurate, traceable total ozone column measurements and Umkehr ozone distribution observations. The total ozone results are archived along with other ER-2 data products on the NASA/Ames file server and published on the mission CD-ROM.

Summary of Progress and Results

The CPFM instrument was flown on all of the full-payload flights during the POLARIS deployments (1997) and the ACCENT fall (1999) deployment. Scientifically useful results were obtained during virtually all of the flights. Because of the nature of the CPFM investigation, which contributes a rather different kind of information to the program than the other sensors on board the aircraft, even the less successful flights have still provided valuable insights into the chemistry of the stratosphere.

Several very illuminating results that have come from the deployment of the CPFM along with the chemistry instrument complement during these missions. These include: 1) the verification of the approximate, absolute magnitude and variability of the J-values for ozone photolysis to produce excited molecular oxygen ($O(^1D)$), and the J-value to photolyze NO_2 to produce NO at the aircraft position; 2) the provision of accurate and precise albedo information for chemical modeling; and 3) total ozone column amounts measured from the ground and above the aircraft flight track [McElroy *et al.*, 1996]. The analyses of these results have demonstrated the absolute necessity for collecting radiation data along with the chemical constituent data, since the variability of ozone amounts and albedo along the flight track, and with time, will otherwise add a large unquantified variability to the chemical model calculations. The importance of this conclusion has been demonstrated in several publications (1-5,9,10 below) resulting from the POLARIS project.

The CCD TV camera which is flown along with the CPFM instrument has provided valuable insights into the relationship between the various radiation fields sampled by space-based and *in situ* instruments and the concentrations of atmospheric constituents which the chemical processes in the stratosphere and troposphere control. In particular, significant modeling errors were identified which result from the limited accuracy (~10%) of the TOMS total ozone data fields for SINGLE observations, caused by inadequate knowledge of the true cloud conditions at the location of the aircraft in the TOMS data analysis process.

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Upper Tropospheric-Lower Stratospheric Aircraft *In Situ* Ozone Measurements

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Research Objectives

The objective of this program is to measure ozone concentrations in the upper troposphere and lower stratosphere using a dual-beam ozone absorption photometer. The instrument consists of a mercury lamp, two sample chambers that can be periodically scrubbed of ozone, and two detectors that measure the 254-nm radiation transmitted through the chamber. The ozone absorption cross-section at this wavelength is accurately known; hence, the ozone number density can be easily calculated. At a one-second data collection rate, the minimum detectable concentration of ozone (one standard deviation) is 1.5×10^{10} molecules/cm³ (0.6 ppbv at STP). The instrument has a long and successful history of lower stratospheric measurements on the NASA ER-2 platform and was recently integrated on the NASA WB-57 extending research capabilities to upper tropospheric *in situ* ozone measurements.

Summary of Progress and Results

Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) Summary for NOAA Aeronomy Lab Ozone Photometer: The instrument performed well during all 25 flights beginning with the April 22, 1997 survey flight south from Ames and ending with the return ferry flight from Barber's Point on September 25, 1997. The only instrument problems encountered were on a few flights out of Fairbanks, when about 5 minutes of data were lost due to data system failure. On these flights the pilot noticed the fail light was lit and restarted the instrument using the pilot's instrument control panel. These failures could not be duplicated on the ground and their source has not been determined.

POLARIS I: It was hoped that remnants of the extensive polar ozone loss that had occurred within the 96-97 Arctic vortex might be observed in late April. Although evidence for loss was found in the ozone - N₂O data, extensive loss was not, due in part to the position of the region of high PV (the vortex remnant) which was not accessible to the ER-2. Additionally, based on previous Arctic missions (AASE and AASE II) the flight levels of the ER-2 may have been too high to observe the region containing the greatest evidence for previous ozone loss (below 440 K). There was one dive to 400 K during Polaris I, that being the flight of April 26 with a dive near the pole. During this flight, the most convincing evidence for previous ozone loss was

observed, particularly between 400 K and 470 K. Except near Fairbanks (takeoffs and landings), flight profiles otherwise remained above 440 K.

POLARIS II: Ozone-N₂O distributions were very different from those found during other seasons and from those found at other latitudes. At the upper theta levels, ozone was generally much lower than observed during any other season, and in particular during POLARIS I. This was not so evident at the lowest levels (<420 K). N₂O values were also very low at the upper levels. Some combination of summertime ozone loss combined with the 96-97 polar losses and local isentropic mixing most likely account for these distributions rather than dynamical processes alone.

POLARIS III: The average values for N₂O have increased substantially above 460 K and ozone has increased about 10% relative to N₂O at all levels. The changes in the ozone-N₂O distributions may be explained by decreases in summertime loss rates and isentropic mixing of mid-latitude air (higher ozone and N₂O) with the high-latitude air observed during POLARIS II. The ferry flight to Barbers Point encountered tropical air at about 38°N and the ER-2 remained in tropical air during the remainder of the flight. The flight to the equator was entirely in tropical air with ozone-N₂O distributions virtually identical to those found during OMS-Brazil on February 14, 1997.

The WB-57 Aerosol Mission (WAM) Summary : There were seven WB-57 flights of 6+ hour duration from Houston, four south and three north, during April and May 1998. The flights, some along the tropical tropopause, ranged in altitude from 13.5 to 19 km at latitudes from 9°N to 47°N. All three northbound flights encountered high PV air, particularly that in April. Cyclonic circulation associated with the Arctic vortex persisted at 70 mb until early June with frequent peel-off. The ozone instrument was successfully integrated on the WB-57 platform and performed well for all flights. Ozone mixing ratios were extremely variable in the mid-latitudes, as suggested by PV maps and the longevity of the Arctic vortex below 50 mb. Maximum mixing ratios were 2 ppmv at about 430 K potential temperature. In the tropics, it was often the case that the ozone was 100-200 ppbv in the upper troposphere.

Atmospheric Chemistry of Combustion Emissions Near the Tropopause (ACCENT) Summary: During the first phase of ACCENT (April 1999) ozone measurements were made as part of a collective payload on the WB-57 platform in an effort to address the assessment of aircraft and rocket activities in the upper troposphere and lower stratosphere. The ozone instrument performed well during all flights. For the rocket plume encounters the data analysis software was rewritten to handle the rapidly changing, highly variable ozone levels. Ozone loss was measured in the stratospheric plume wakes of a Delta and Atlas II rocket. Ozone concentration in the center portion of the plume wake was less than 1% of the unperturbed, local background value. The ozone loss exceeded the amount predicted by models of gas phase chlorine chemistry for solid propellant rockets demonstrating that gas or particulate emissions from the kerosene fueled component of the propulsion systems destroys ozone.

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Differential – Absorption IR Measurements of CO, CO₂, CH₄, N₂O, and H₂O_(v)

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Research Objectives

The key scientific objective of this program is to assess how nitrogen oxides (NO_x), CO, and hydrocarbons emitted from subsonic aircraft, as well as less understood heterogeneous processes, may perturb upper tropospheric/lower stratospheric (UT/LS) ozone. Tracer measurements are essential for thoroughly documenting the composition and sources of air within and adjacent to heavily traveled flight corridors for assessment of aircraft emission-induced differences. A secondary objective is to address how the emission of water vapor and particulates by aircraft perturbs clouds and aerosols thus modifying UT/LS radiative forcing and global temperature. Fast-response CO₂ measurements are required to generate emission indices (EI) for other trace species measured within aircraft plumes.

Summary of Progress and Results

DACOM (Differential Absorption CO Measurement) flew successfully on all fourteen science flights conducted as part of the SONEX (Subsonic assessment, Ozone and Nitrogen oxides EXperiment) campaign which investigated the atmospheric impact of commercial air traffic within the North Atlantic Flight Corridor. Signatures of aircraft emissions within the corridor were observed infrequently during the mission in our tracer data. There were only two cases where enhancements in the CO data could be attributed to intersecting aircraft plumes (EIs commensurate with those of modern aircraft engines) and eight instances where a concomitant increase in CO₂, NO_y, and condensation nuclei was observed (possible indicator of aircraft corridor). No detectable changes in CH₄ or N₂O were realized during these respective time periods.

Recent satellite observations have shown that condensation trails (contrails) generated by aircraft can persist evolving into extensive cirrus clouds possessing the potential to alter the Earth's radiation balance. This evolution from contrails to cirrus sheets occurs in regions where the atmosphere is highly saturated with respect to ice. Water vapor mixing ratios, as determined by our instrumentation, were used to calculate the prevalence of these ice saturated conditions which accounted for 8.6% of the UT data obtained suggesting a possible minor radiative effect from contrails within the SONEX sampling region.

The largest enhancements in the tracer data during the mission emanated from source regions within the continental United States. Back-trajectory analyses indicated that these pollution plumes were advected out over the Atlantic Ocean and transported intact over long distances within the lower to mid-troposphere in well defined layers for thousands of kilometers.

Publications

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Atmospheric Photolysis Frequency Measurements During the NASA SOLVE Mission

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Research Objectives

Photochemical reactions provide the driving force for much of the chemistry in the atmosphere. The *in situ* rates of these photolysis reactions are important in understanding production and loss terms for ozone and cycling of atmospheric nitrogen oxide species. The objective of this proposed research is to measure spectrally resolved down welling and upwelling actinic flux aboard the NASA DC-8 during the SOLVE missions in 1999-2000. Photolysis frequencies for 11 atmospheric species O₃, NO₂, CH₂O, HONO, HNO₃, CH₃NO₃, CH₃CH₂NO₃, H₂O₂, CH₃OOH, CH₃COCH₃, and PAN will be calculated from the measured spectral actinic flux and a variety of molecular data. The PIs will use the expertise gained in making aircraft measurements on the DC-8 during PEM-Tropics A, SONEX, and the upcoming PEM Tropics B mission in addition to our experience with ground-based photolysis frequency measurements. It is anticipated that the improved instrumentation will have a detection limit less than 1×10^{-8} sec⁻¹ for JO(¹D) and 3×10^{-8} sec⁻¹ for JNO₂ with a time resolution of 10 seconds.

Summary of Progress and Results

Currently, instruments are being tested and calibrated before installation on the DC-8 in October. This includes angular response testing, wavelength calibration stability, and spectral response stability. Data acquisition and instrument control software is being upgraded. The data reduction software is being upgraded to calculate photolysis frequencies for additional molecules that are of interest to SOLVE investigators.

Publications

None

Physical and Chemical Properties of Aerosols and Cloud Particles: Ames Wire Impactor Applications

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Research Objectives

Recent modeling studies have suggested a link between BCA (Black Carbon Aerosol) and ozone chemistry via the reduction of nitric acid, nitrogen dioxide, and ozone on BCA particles. The ozone reaction converts ozone to oxygen molecules, while nitric acid can react to form NO_x. Also, a buildup of BCA could reduce the single-scatter albedo of aerosol below a value of 0.98, a critical value that has been postulated to change the radiative effect of stratospheric aerosol from cooling to warming. Correlations between measured BCA amounts and aircraft usage have been reported. Attempts to link BCA to ozone chemistry and other stratospheric processes have been hindered by questions concerning the amount of BCA that exists in the stratosphere, the magnitude of reaction probabilities, and the scarcity of BCA measurements. Our primary objectives as part of the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission were: (1) to determine the distribution of sulfate and soot aerosols, and (2) to determine the role of these aerosols in stratospheric photochemistry.

Measurements of aircraft plumes indicate that aircraft emit substantial numbers of volatile and nonvolatile particles during flight. These observations have caused concern that commercial aviation sources may significantly impact heterogeneous processes, cloud formation, and microphysics in the upper troposphere and lower stratosphere. As part of the Subsonic Assessment Ozone and NO_x Experiment (SONEX) our objectives were to measure the distribution of aerosol and cloud during the mission, to determine the fraction of total aerosol that can be attributed to aircraft-generated sulfur, and determine the relevance of this aerosol as a marker of aircraft influenced air and its effects on the regional climate.

Summary of Progress and Results

To facilitate our measurements, a system that automates the operation of the Ames Wire Impactors was designed, fabricated, and flown successfully on POLARIS. This system alleviates the pilot workload immensely and allows the experimenter the flexibility to sample at predetermined altitudes, locations, or temperatures.

Because of the fractal nature of BCA, modification to the AWI data analysis procedures was required in which the collection of BCA is modeled as a fractal aggregate. The new method results in an increase in the measured BCA surface area of about fifteen times and an increase in soot loading of about six times over the previously used approach. Despite this increase, BCA surface area is only about 10% of the measured sulfuric acid aerosol surface area.

Including heterogeneous reactions on BCA in a photochemical model can effect photochemistry leading to renoxidation and increased ozone depletion. However, these predicted effects are not supported by the POLARIS observations, in particular the NO_x/NO ratios. Including BCA reactions does not statistically improve the agreement between model and measurement in any of the several scenarios considered. Furthermore, if the reactions cause even partial carbon oxidation, the BCA would be consumed at a rate inconsistent with POLARIS observations. These inconsistencies lead us to conclude that the presence of BCA in the stratosphere did not affect stratospheric photochemistry during POLARIS.

An instrument, based on the thermal volatilization of aerosols, was fabricated and flown on the SONEX mission to discriminate sulfuric acid, ammonium sulfate/bisulfate, and nonvolatile aerosols during the mission. Using this instrument, a significant increase in the sulfuric acid aerosol was observed under conditions where other indicators suggested that the air parcels were influenced by aircraft exhaust. The bulk of these occurrences were above 9 km altitude. The sulfuric acid aerosol do not appear to measurably affect surface area and volume of the background aerosol due to their small diameter, and therefore do not appear to affect radiative transfer directly. Only a very small fraction of the nonvolatile aerosol could be identified as BCA.

Publications

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Free Radical Measurements from the DC-8 Aircraft

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Research Objectives

This project is to deploy a new instrument for *in situ* measurements of halogen oxides in the troposphere and high-latitude lower stratosphere on the NASA DC-8 aircraft during the SOLVE mission. ClO and BrO could enhance ozone destruction in the upper troposphere in regions that are NO_x-deficient. UARP support will be used to modify an existing lightweight, autonomous instrument, and integrate it into the low-pressure flow system of the ATHOS instrument that presently flies on the NASA DC-8, an instrument designed and built by Professor William Brune at Penn State. Two detection modules, one to measure chlorine atoms and the other to measure bromine atoms, will be integrated downstream of the OH/HO₂ LIF detection module of ATHOS. Halogen atoms will be detected at part-per-trillion abundances in a sample of tropospheric air following conversion by addition of nitric oxide. This conversion will take place at low pressures required for adequate transmission of vacuum ultraviolet emission from plasma lamps maintained by a radio-frequency discharge of helium at 180 MHz. When operated in a similar mode for the ground-based Arctoc '96 campaign in Ny Alesund, Spitsbergen in April and May 1996, the instrument demonstrated an ultimate detection limit of sub-ppt for both chlorine and bromine with signal averaging, and 3-4 ppt point-to-point (20 second) precision. This instrument has a heritage that includes a half-dozen successful flights on small balloons, several weeks of measurements in the high-latitude boundary layer, and over 20 successful flights of the NASA WB-57 aircraft, including three into the plumes of rockets.

Summary of Progress and Results

This is a new project that just recently received FY99 funding. In several months since the start of this project we have ordered new vacuum ultraviolet photomultiplier tubes that will be repackaged to meet DC-8 specifications, and an autoranging AC input, DC/DC converter to operate at 400 Hz aircraft power. The electronics from the WB-57 instrument will be repackaged to combine the computer, power supply, distribution panels, and lamp controllers into one small electronics package suitable for rack-mounting with the ATHOS electronics. The instrument will weigh approximately 50 pounds. We have tested a complete detection module with the LIF system at Penn State and found no detectable RF interference. The final instrument will be integrated into the ATHOS flow system and DC-8 rack in the beginning of October 1999 at Penn State and integration onto the DC-8 will take place later that month. The first test flights are scheduled for the second half of November.

Publications

None

CIMS Measurements of Atmospheric Nitric Acid

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Research Objectives

The objective of the AFRL research has been to make fast, accurate measurements of concentrations of sulfur dioxide and nitric acid in the upper troposphere and the lower stratosphere. HNO_3 is a reservoir species for NO_y and relevant to the problem of ozone depletion. SO_2 is a tracer for sulfur and is the principal component of SO_x . A chemical ionization mass spectrometer (CIMS) system was designed for fast response in order to measure trace gas concentrations during aircraft and rocket plume encounters.

Summary of Progress and Results

A chemical ionization mass spectrometer (CIMS) has been flown on a number of missions:

The CIMS instrument was mounted inside a NASA T-39 aircraft outfitted for close chases in the plumes of other jet aircraft, for the SNIF-1, 2, and 3 campaigns during the years 1995-1997. The SNIF-3 program (June 1997) focused on flights behind F-16 fighter aircraft from New Jersey and Vermont Air National Guard Units. The F-16s separately carried fuels of different sulfur level. The F-16s successively pulled ahead of the T-39, at an altitude typically 11 km, and separation distances of 0.1-3 nautical mile, for exhaust plume measurements under low and high power conditions. The SO_2 mixing ratios observed in the plumes relative to plume CO_2 measurements by NASA were found to be consistent with low S(IV) to S(VI) conversion and independent of plume age.

The CIMS instrument was flown on a NASA DC-8 for the SONEX campaign of the fall of 1997, studying air traffic corridors principally over the North Atlantic, in the troposphere (altitudes from 6-12 km). Combining HNO_3 measurements with data obtained by others during SONEX, HNO_3 was found to represent 30-80% of the NO_y in the upper troposphere. The normal mixing ratio of HNO_3 in the upper troposphere was not much larger than the CIMS background ion signal (background related to ion hydration). However, on a number of occasions the DC-8 flew through regions of high potential vorticity where stratospheric air mixed with tropospheric air. In these regions, HNO_3 mixing ratios 3-6 times greater than normal were measured.

The mass spectrometer instrument was mounted in the bomb bay of a NASA WB-57 aircraft for the Air Force RISO program (1996-1999). The WB-57 was flown through the exhaust plumes of

solid and liquid fueled rocket motors (the space shuttle, Deltas, and Titans) at altitudes around 19-km. For solid fuel rockets, measurements of HCl, Cl₂, and ClO concentrations in the plumes were made. The results of the measurements have been used for modeling the evolution of chlorine-containing compounds as they undergo photolysis and the local effect of these species on ozone. Chemical ionization detection of HNO₃ has recently been accomplished for one set of plume crossings in association with the RISO/ACCENT program.

In addition to the flight studies, the CIMS instrument was used to measure SO₂ and HNO₃ concentrations at the exhaust plane of an F-100 jet engine (from an F-16 fighter aircraft) mounted in an altitude simulation chamber at NASA-Glenn Research Center, during August and September 1997. Jet A fuels with different sulfur content were used in the tests, as well as JP-8 fuel with a medium-sulfur level. The CIMS results showed that most (>85%) of the fuel sulfur appeared as gaseous SO₂ in the engine exhaust, quite independent of engine power, altitude, and fuel type. In contrast, the HNO₃ produced in the engine decreased precipitously with engine power, presumably because of the thermal instability of HNO₃. Comparing these data for HNO₃ with measurements of NO and NO_x made by the NASA-Glenn group, we deduced the efficiency of conversion of NO₂ into HNO₃ in the F-100 engine. The NO₂→HNO₃ conversion rate varied from about 8% at engine idle to as low as 0.1% at cruise power, depending on altitude. These measurements of HNO₃ were the first to be made at the exhaust plane of a jet engine. The low efficiency for HNO₃ production determined in this work is consistent with our *in situ* measurements behind jet aircraft.

Finally, AFRL has carried out considerable laboratory research in support of the CIMS aircraft work. Flow tube apparatuses have been used to measure reaction rates for chemical ionization detection of SO₂, SO₃, H₂SO₄, and ClONO₂ as well as reaction rates for important atmospheric electron and ion processes. Four representative publications are included below for the laboratory work.

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Aircraft Measurements of the ALIAS Instrument

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Research Objectives

The Aircraft Laser Infrared Absorption Spectrometer measurements task has as its primary objective the collection of data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere and troposphere. The *in situ* laser absorption spectrometers ALIAS (ER-2) and ALIAS-II (balloon) provide measurements of several gas concentrations as part of multi-instrument aircraft and balloon payloads flown for NASA missions, and for satellite correlative measurements, e.g., the Upper Atmospheric Research Satellite (UARS) and the Stratospheric Aerosol and Gas Experiment (SAGE III). The instruments use tunable diode lasers in the 3-10- μm wavelength region to measure gas concentrations in multi-pass optical cells either contained in a flow vessel (ALIAS) or in an open-path deployed cradle (ALIAS-II). The instruments have demonstrated capability for N₂O, CH₄, HCl, CO, and NO₂ at the tens-of-parts-per-trillion levels, with capability to measure other gases within the 3-20- μm wavelength region. ALIAS is a 4-channel instrument, ALIAS-II is a 2-channel instrument.

Summary of Progress and Results

Over the last three years, the ALIAS instrument has flown as part of the payload of the ER-2 aircraft in two major missions: the 1997 Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission out of Moffett Field, California, Hawaii, and Fairbanks, Alaska, and the 1999 Tracer Intercomparison Experiment for SOLVE (TIES) out of Dryden, California.

During POLARIS, the ALIAS instrument produced simultaneous measurements of N₂O, CH₄, CO, and HCl, sampling the latitude range 0 - 90°N, over the region from the upper troposphere to lower stratosphere in flights out of California, Alaska, and Hawaii. The instrument performed very well during all three phases of the POLARIS deployments, producing data on 23 out of 24 flights, and with complete data sets for all four gases on about 75% of those flights. The POLARIS mission offered the opportunity to extend the CH₄ vs. N₂O correlation data base and further determine to what extent the tracer-tracer relationships can be used to characterize air masses and distinguish tropical, mid-latitude, and vortex air. This framework provides a reference frame for quantitatively determining the rates of transport and mixing between different regions of the stratosphere and between stratosphere and troposphere. The ALIAS N₂O

measurements were compared with those from ATLAS and ACATS during many of the flights. In addition, ALIAS CH₄ data were compared with those from ACATS. All three N₂O measurements and the two CH₄ measurements agreed better than in previous missions. Least-squares fits to the N₂O data show high correlation (>0.95) between ALIAS/ATLAS/ACATS measurements; one-sigma standard deviation between ALIAS/ATLAS N₂O is about 6 ppbv (2%) with systematic differences in slope/intercept of less than 4%. The ACATS measurements correlate similarly with ALIAS and ATLAS, showing deviations of about 10 ppbv (3%) and slope/intercept differences of less than 3%. The ALIAS and ACATS measurements of CH₄ show excellent agreement (correlation coefficient 0.98), with one-sigma standard deviations of about 2%, and slope/intercept differences of a similar amount. There is a tendency for ACATS measurements of tropospheric CH₄ to be higher than those of ALIAS.

During the POLARIS mission, the ALIAS CO data base was extended in time and season, with data quality comparable to, or higher than, previous missions. The CO data set from the ER-2 is now extensive enough that mean mixing ratio contours are being generated and compared with 2-D model simulations to identify the dependence of its production and loss terms on latitude and altitude, where seasonal dependences can clearly be extracted. ALIAS CO over Alaska had a very sharp gradient at the tropopause, typically starting at 80-115 ppbv 0.5 km below the tropopause and decreasing to only 30-40 ppbv 1.0 km below the tropopause. This reflects the lack of aerosol across the high latitude tropopause. Although the minimum in the CO tropospheric seasonal cycle nominally occurs in July to August at mid- and high- latitudes, extremely high CO (up to 180 ppbv) was observed in the upper troposphere in June and July POLARIS flights due to forest fires. At potential temperatures greater than 480 K, CO is in photochemical steady-state with mixing ratios ranging from 10 to 15 ppbv, depending on the temperature history. On the southern survey flight of 970923, the CO mixing ratio was approximately 60 ppbv at the tropical tropopause. This is consistent with the observed CO during the STRAT southern surveys. Carbon monoxide is a sensitive probe of air which has been in the stratosphere for less than 6 months or so, and we are using it as a tool for understanding atmospheric transport from the tropics to mid-latitude lower stratosphere. In model calculations, the photochemistry of CO along the flight-track is constrained by simultaneous measurements of CO and CH₄ by ALIAS, OH by the Harvard HO_x instrument, NMHC by the NCAR WAS experiment, and model Cl and O(¹D) from the PS files of Salawitch.

ALIAS provided excellent HCl data throughout most of the POLARIS mission. The agreement between the ER-2 ALIAS HCl measurements and those of the balloon MarkIV FTIR instrument flown at similar times from Alaska is excellent, and gives confidence in our ability to extend the aircraft data sets to higher altitudes where appropriate. With the new ClONO₂ measurements of Harvard University, the POLARIS mission provided the first opportunity to test the inorganic chlorine partitioning from simultaneous measurements of ClO, ClONO₂ (Harvard University) and HCl (ALIAS). Initial results show that the agreement between the sum ClO+ClONO₂ +HCl and the measured Cl_y is remarkably good. In flights where the ClONO₂ varies as expected, the HCl is seen to compensate to maintain the integrity of the sum. HCl vs. N₂O correlations were captured for the low background aerosol conditions characteristic of POLARIS. The mid-latitude HCl measurements show HCl/Cl_y values of about 70-80% that are consistent with low-aerosol data from earlier missions, and contribute to the long-term data base that indicates an HCl/Cl_y ratio increasing with time as the aerosol loading diminishes.

During the September 1999 TIES mission, ALIAS participated in three flights aimed at intercomparison of N₂O and CH₄ data collected from several ER-2 instruments, ALIAS, ATLAS, ARGUS, and ACATS. In addition to N₂O and CH₄, ALIAS also measured CO₂, CO, and HCl. This was a milestone flight series for ALIAS and for the measurement community in that for the first time ever, a quantum-cascade (QC) laser was flown to make atmospheric measurements. This flight series also demonstrated the practicality for SOLVE of using CO₂ measurements for in-flight calibration.

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NO and NO_y Measurements in the Stratosphere

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Research Objectives

Reactive nitrogen species are important to the chemistry of O₃ throughout the atmosphere. We are interested in the measurement of NO, NO_y, and O₃ in the upper troposphere and lower stratosphere, especially, where reactive nitrogen species have not been thoroughly measured, yet where they may be subject to the influence of aircraft emissions. This is also a region where NO_x is relatively long-lived, so sources such as aircraft and lightning, which are present in this region but which are not large in terms of overall magnitude, can have a disproportionate effect. Among the topics we address with our measurements are the following: near-field exhaust studies, heterogeneous interconversion among NO_y species, the abundance of particulate NO_y, lightning as a source of NO_x, and the climatology of NO_x and NO_y. Also, there are issues surrounding the measurement of NO₂ and NO_y, and these are addressed with laboratory studies and in-flight diagnostic tests.

Summary of Progress and Results

Our work during this period consisted of analyzing data from TOTE/VOTE and SUCCESS, which occurred in 1995-1996:

Campos *et al.* [1998] analyzes near-field exhaust measurements behind a Boeing 757. For plumes aged 20-300 seconds at 37 kft altitude, the average NO emission index is 7.7 g NO₂/kg fuel, and measured indices are frequently higher than predicted. About 95% of the emitted NO_y was found to be in the form of NO_x (NO₂ calculated from measured NO).

Weinheimer *et al.* [1998] analyzes condensed-phase NO_y observed in the wave cloud of 960502. Simultaneous forward- and aft-facing NO_y inlets were used to infer the amount of condensed-phase NO_y present on ice particles that were up to a few minutes old. Particulate amounts were 25-75 pptv, or 10-20% of gas phase NO_y. Given the rapid HNO₃ uptake on ice observed in the laboratory, a model calculation implies that virtually all of the gas phase HNO₃ will be depleted in the first 1-2 minutes after the appearance of ice. Thus the NO_y observations are consistent with the laboratory results only if the ambient HNO₃/NO_y ratio is 10-20%.

Jaeglé *et al.* [1998a] addresses the origins of NO_x in the upper troposphere over the central United States. Correlations between NO_y and CO suggest that NO_x originates primarily from the convective transport of polluted boundary layer air. Steady-state model calculations constrained by local observations of NO and other species underestimate the measured NO_x/NO_y

concentration ratio by a factor of two on average; the discrepancy decreases with decreasing concentrations of condensations nuclei, which we take as a rough proxy for the age of air in the upper troposphere. We conclude that the long lifetime of NO_x in the upper troposphere (5-10 days), combined with the frequent supply of fresh NO_x from convection of polluted boundary layer air, could explain the observed NO_x/NO_y ratio. In contrast to previous studies, the observations obtained during SUCCESS do not offer evidence for fast heterogeneous recycling from HNO_3 to NO_x .

Jaeglé *et al.* [1998b] addresses the sources of HO_x and the production of O_3 in the upper troposphere over the United States. The HO_x concentrations measured in SUCCESS are up to a factor of 3 higher than can be calculated from oxidation of water vapor and photolysis of acetone. The highest discrepancy was seen in the outflow of a convective storm. The convective injection of peroxides from the boundary layer to the upper troposphere can resolve this discrepancy. The OH and HO_2 observations together with the observations of NO allow us to directly calculate the ozone production in the upper troposphere and its dependence on NO_x . We find an average net ozone production of 2 ppbv day⁻¹ between 8 and 12 km over the continental United States in the spring. Ozone was NO_x -limited under essentially all the conditions encountered in SUCCESS. The high levels of HO_x present stimulate ozone production and increase the sensitivity of ozone to NO_x emissions from aircraft and other sources.

Brune *et al.* [1998] addresses background HO_x levels in the cloud-free troposphere and lower stratosphere. NO is critical to the partitioning of HO_x into OH and HO_2 via its reaction with HO_2 , converting HO_2 to OH. Measured HO_2/OH ratios are in reasonable agreement with those modeled. At ratios less than 20, which occurred above the tropopause, the observed ratio is about 30% larger than the modeled ratio. Because NO dominates the conversion of HO_2 to OH for much of the lower atmosphere, the HO_2/OH ratio is expected to be approximately inversely proportional to the NO mixing ratio, and this is borne out by the measurements.

Tan *et al.* [1998] focuses on HO_x measurements in exhaust plumes. The behavior of HO_x in exhaust plumes is still not well understood. In particular, there is more HO_2 than expected, since the very high NO levels are expected to reduce HO_2 to essentially zero, and this is not observed. Also, the measured and calculated HO_2/OH ratios do not agree well with one another, as they do outside exhaust plumes.

Weinheimer *et al.* [1998] compares species measurements from the DC-8 and ER-2 during their respective VOTE and STRAT campaigns. The measurements compared are those of NO, NO_y , O_3 , CO_2 , CH_4 , and N_2O . The comparisons were generally favorable.

Weinheimer *et al.* [1998] addresses the interference to NO_y measurements due to HCN. During TOTE/VOTE and SUCCESS we measured the in-flight HCN conversion efficiency about every other flight. For SUCCESS these are the results for the aft-inlet NO_y measurement: The range for the HCN conversion efficiency was 1.2-7.5%, the mean was 4.2%, and the median was 4.8%. Thus a representative NO_y overestimate would be 5% multiplied by an estimated HCN mixing ratio of 200 pptv, or 10 pptv. This is usually small (<10%) relative to ambient NO_y mixing ratios. At times the measured mixing ratio is below 100 pptv, and for such cases this interference is of greater concern.

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Development of an Aircraft-Borne Instrument for Measurement of Nitric Acid

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Research Objectives

The composition of atmospheric aerosols governs their radiative and chemical properties. Understanding and modeling these properties, however, has been significantly hindered by the lack of quantitative, and often even qualitative, information about the phase and composition of atmospheric particulate. With support from NASA, NSF, and NCAR, and Caltech, we are developing an autonomously-operated airborne instrument to characterize the composition of aerosol and cloud particles in the upper troposphere and lower stratosphere (UT/LS). Combined with a measurement of the gas phase concentration of these semi-volatile compounds (such as nitric acid) this instrument will provide a powerful data set for investigating the photochemistry of the UT/LS.

Summary of Progress and Results

In this collaborative effort between the California Institute of Technology and the National Center for Atmospheric Research we are coupling the selected ion chemical ionization technique with a novel impactor inlet. Using inertial separation techniques, we will selectively exclude either the gas or condensed phase from our sample. After warming, we will detect semi-volatile acids with sensitivity greater than 50 pptv. Our initial effort is focused on determining the nitric acid concentration in both the condensed and gas phase.

This development project has been underway for just over 15 months. We will participate in test flights in October 1999. Following these tests, we will deploy the instrument to northern Scandinavia in January to March 2000 as part of the upcoming NASA-sponsored campaign to study the chemistry of the polar winter stratosphere.

Publications

None

Aerosol Measurements from the ER-2: Upgrade of the Focused Cavity Aerosol Spectrometer and Its Sampling Inlet

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Research Objectives

The research objective was to make measurements that contribute to better understanding of the impact and evolution of the aerosol in the upper troposphere and lower stratosphere. During the period, measurements of aerosol properties were made from the NASA ER-2 aircraft in STRAT (Stratospheric Tracers of Atmospheric Transport), and in POLARIS (Photochemistry of Ozone Loss in the Arctic Region in Summer). Measurements were also made from the NASA WB-57f in WAM (WB57 Aerosol Measurements).

Summary of Results and Progress

Measurements were made of the concentration of condensation nuclei (particles larger than 8 nm) and of aerosol size distributions in the size range from 90 to 2000 nm during these three deployments. Condensation nuclei were counted with the ER-2 CNC II and the size distributions were measured with the FCAS II (Focused Cavity Aerosol Spectrometer). Data have been reported for 43 flights during the period covered by this report.

Extinctions calculated from the measured size distributions have been compared with those measured by the SAGE satellite. Comparisons were made for measurements that were nearly co-located in space and time. Approximately 70 points were compared for the time interval covered by this report. Figure 1 is a plot of the extinctions calculated from the FCAS size distributions against the SAGE measurements. The fractional deviations of the FCAS extinctions from the SAGE were calculated. The median of these fractional deviations is 10%. The median of the absolute values of the deviation is around 20%. Extinctions were calculated for the four SAGE wavelengths. These comparisons show that the *in situ* and remote determination of extinction correlate well and that most values agree within 25%.

Aerosol surface values were used in studies of heterogeneous chemistry. The trends in aerosol properties as the effects of the Pinatubo eruption waned and the details of size distributions of stratospheric aerosols have also been studied and reported at meetings. Papers are being prepared describing the results of the aerosol studies.

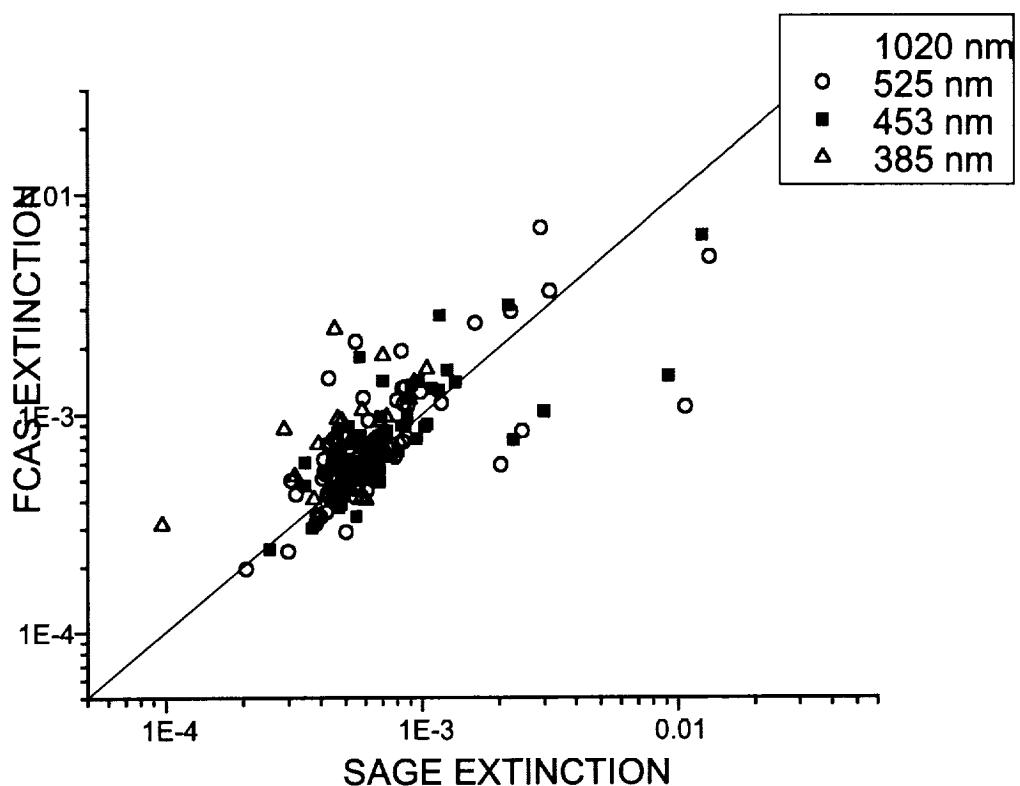


Figure 1. Optical extinction at the SAGE wavelengths calculated from the FCAS size distributions. The FCAS and SAGE measurements were nearly co-located.

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Aircraft CO₂ Measurements

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Research Objectives

The objectives were (1) to measure time series for CO₂ in the lower and middle stratosphere; (2) to use this time series to define the propagation of the tropospheric seasonal cycle and long-term trend of CO₂ into the stratosphere; and (3) to analyze the results from (2) to provide detailed information about transport rates throughout the stratosphere.

In the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS, 1997, 2°S to 90°N) experiment the general goal was to continued the time series of high-accuracy CO₂ measurements obtained previously (1992-1996) from ER-2 missions. Specific objectives for the mission focused on determining changes in the mean age of air in the polar stratosphere during the summer season, to define the contributions of transport to changes in ozone. We also examined exchange of air between the tropics and high latitudes, and measured the vertical propagation and attenuation of the seasonal cycle in the tropics during northern summer for the first time.

Summary of Progress and Results

We obtained excellent measurements of CO₂ on all 41 flights of POLARIS, and also on two flights of opportunity from NASA Dryden in November 1998. We observed CO₂ in air that had recently entered the stratosphere (as indicated by simultaneous observations of N₂O, H₂O, CO, and potential temperature) during both April and September 1997, and November 1998, extending our record of the stratospheric boundary condition for CO₂. We did not encounter air that had recently entered the stratosphere during the June/July deployment, suggesting that the polar stratosphere was effectively isolated from lower latitudes during that time.

Mean ages were derived from the time lag between observed CO₂ values (corrected for CH₄ oxidation), using our observed stratospheric boundary condition for CO₂. During April/May 1997 mean ages up to 5.5 years were observed during a flight into the edge of the polar vortex, while mean ages up to 5.8 years were observed in remnants of the vortex encountered during

June/July 1997. The increase in age between the two deployments could be attributed to the passage of time in effectively isolated air, within 1 month, suggesting that the air mass was not significantly diluted by mixing with either older or younger air during this time period. This hypothesis is consistent with the fact that the remnants of the polar vortex persisted several months after the breakup of the main vortex. Measurements of CO₂ to 32 km obtained on June 30, 1997 using a high-altitude balloon, showed that air with mean ages up to 6.5 years was present aloft. By September 1997, the vortex remnants had disappeared and the maximum mean age at ER-2 altitudes was only 4.6 years, indicating significant influx of younger air from lower latitudes.

The evolution of relationships among CO₂ and other tracers at ER-2 altitudes during POLARIS showed that, although rates of transport and mixing were slow, loss of O₃ in the lowest 1-2 km of the stratosphere could be largely due to mixing processes rather than photochemical loss. In the vicinity of 20 km it appeared that the effects of photochemistry were comparable to, or larger than, transport, as causes of ozone.

We focused considerable effort on analysis and synthesis of the entire time series of aircraft CO₂ observations, since frequent re-visits to the stratosphere have ended and the acquisition of a high-resolution time series interrupted. We show that the data allow us to derive empirical age spectra for both the tropical and mid-latitude lower stratosphere. [An age spectrum is the probability distribution function of transit times from the tropical tropopause to a particular point in the stratosphere. The mean age corresponds to the first moment of the age spectrum.] The derived age spectra provide a detailed picture of transport process throughout the stratosphere. The tropical age spectra vary seasonally, consistent with faster ascent rates in northern winter as expected if the circulation is being driven by wave-breaking in the extratropics. The mid-latitude age spectra consist of two distinct peaks corresponding to transit times of <1 year and 4-6 years. The younger peak represents rapid quasi-horizontal transport from low latitudes in the region just above the tropopause, while the older peak corresponds to advection by the residual circulation. These results, along with mean ages derived from our tropical and mid-latitude balloon profiles of CO₂, provide stringent tests of transport parameterizations used in numerical models of the atmosphere.

Publications

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E. ROCKET-BORNE MEASUREMENTS



Rocket-Borne Temperature and Wind Measurements

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Research Objectives

Correlative data are obtained and used by the science community for the validation of temperatures retrieved from satellite remote measurements and ground-based lidar. Algorithms for the analysis of the rocketsonde data have been improved. The experimenters of the High Resolution Doppler Interferometer (HRDI) instrument on the Upper Atmosphere Research Satellite (UARS) have taken great advantage of this *in situ* data to tune up the satellite reduction algorithms, as has the WINDII investigators. The rocketsonde data are cataloged on the Upper Air Instrumentation Research Project homepage and data are available, upon request. This effort continues to provide excellent synergism with other NASA investigators, at this time is the only NASA facility having the ability to make such measurements, and the overall program structure is flexible allowing cooperation with experimenters of other Government agencies, and even with investigators from universities and other countries.

Summary of Progress and Results

Rocket-borne instruments are used to obtain observations of high altitude temperature, density, and wind measurements for the validation of NASA satellite remote measurements, lidar temperature validation, and to meet other mission-unique requirements. Rocketsonde launch opportunities are scheduled using the satellite ephemeris information. Validation measurements provided to the instrument scientist of the High Resolution Doppler Interferometer (HRDI) and the Wind Interferometer (WINDI) instruments on the Upper Atmosphere Research Satellite (UARS) were valuable in that these allowed the reduction algorithms to be enhanced, as necessary.

Rocketsonde measurements were obtained in conjunction with UARS/HRDI, UARS/WINDII, and the German CRISTA 2 instrument flown on NASA Shuttle designated STS-85 during 1997. A method to improve small rocket trajectories were adapted from an in-house study leading to improved safety involved with the impact prediction of these systems.

Measurements from the passive inflatable falling sphere have been enhanced significantly because of new, improved data reduction algorithms. A data catalog (not data) is under development to be made available over the World Wide Web.

Stratospheric and-mesospheric measurements of temperature, density, and wind are planned in cooperation with the validation of SAGE III (when on orbit), and other NASA missions as required. An improved wind reduction algorithm for the falling sphere was developed and is in the process of being written for publication.

Rocketsonde measurements obtained from a number of North American launch sites and from launch sites of the Former Soviet Union (FSU) show that trend of stratospheric temperatures is downward, i.e., decreasing at a rate of as high as 2° per decade. Although each site shows a slightly different rate, it is clear that stratospheric temperatures decreased. The advantage of this study is that the rocket instruments used in the United States were the same at all sites, and in the FSU the instruments used at all of the FSU sites were the same. The trend results from both agreed.

Studies of high altitude meteorological dynamics were carried out to better understand wave activity in the atmosphere and the influence of high altitude dynamics on weather in the troposphere.

Publications

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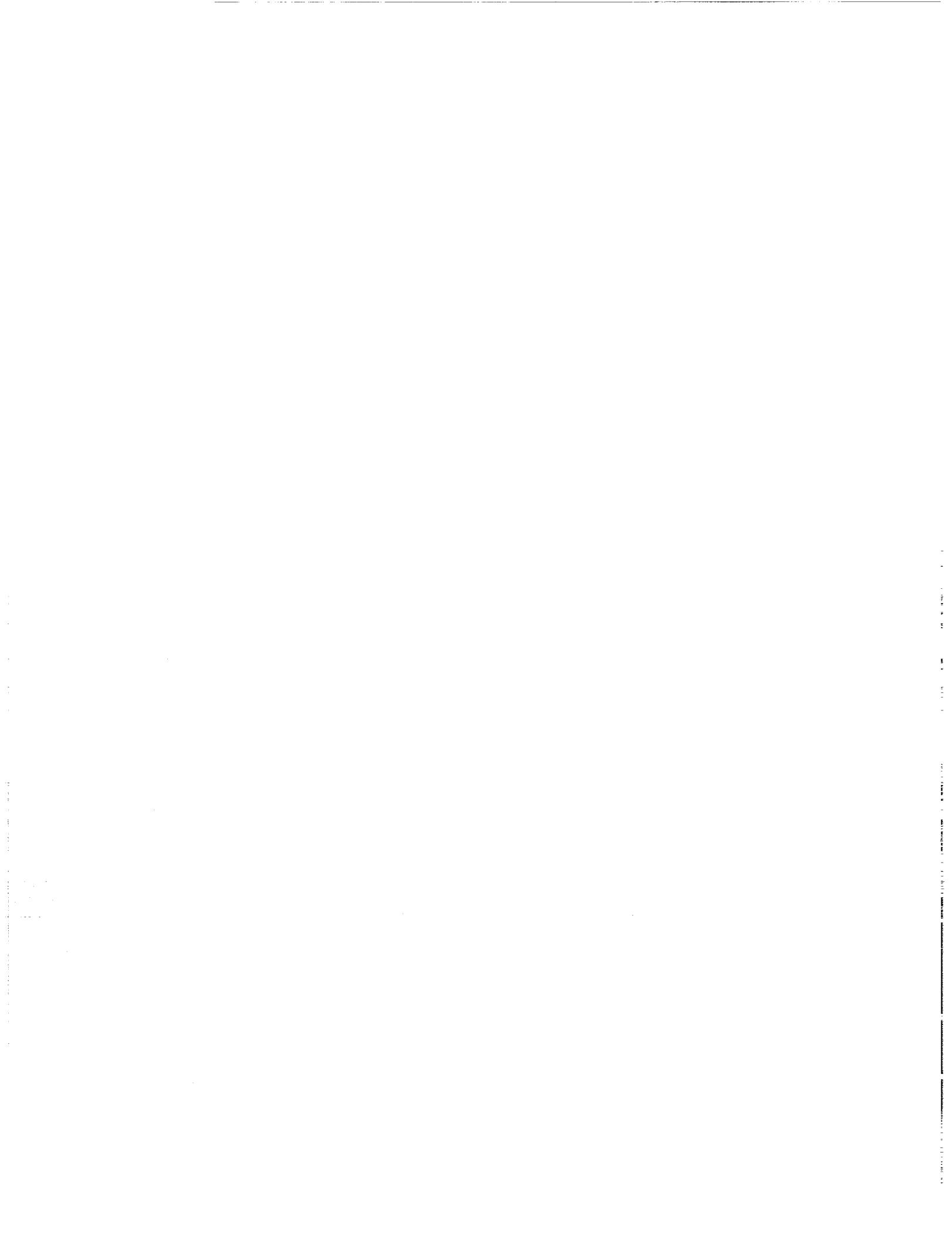
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LABORATORY STUDIES

- A. REACTION KINETICS AND PHOTOCHEMISTRY**
- B. SPECTROSCOPY**



A. REACTION KINETICS AND PHOTOCHEMISTRY



Kinetics and Mechanisms of the Atmospheric Photooxidation of Some Hydrochlorofluorocarbons and Hydrofluorocarbons

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Research Objectives

Laboratory investigations of the kinetics and mechanisms of the atmospheric photooxidation of some compounds that are replacements for the ozone-depleting chlorofluorocarbons in large-scale industrial applications, and of other trace halocarbons, are being conducted. It is important to understand the atmospheric chemistry of these compounds so that the full global scale environmental implications of the presence of these halogenated compounds in the atmosphere can be assessed. We are using flash photolysis with time resolved mass spectrometry for the experimental studies. These are being supplemented with ab initio calculations of molecular structure and energetics, and application of theories of chemical kinetics. These methods provide the tools to determine the importance of various reaction pathways and the ultimate environmental sinks of the chlorine and fluorine carried by these halogenated compounds.

Summary of Progress and Results

Kinetics of the CH₂ClO Radical at 306 K: The gas phase kinetics of the CH₂ClO radical, formed by flash photolysis of Cl₂ in CH₃Cl/O₂/N₂ mixtures, was investigated at 306 K and at total pressures from 5 to 35 Torr by time-resolved mass spectrometry. The bimolecular reaction of CH₂ClO with O₂ to form HC(O)Cl and the unimolecular elimination of HCl were both observed. The absolute rate coefficient for the bimolecular reaction of CH₂ClO with O₂ is $(2.8 \pm 1.2) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The HCl elimination is well into the fall-off.

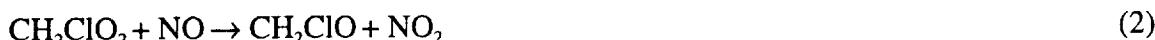
The Temperature Dependence of the Reaction of CH₂ClO with O₂ and NO, and the Unimolecular Elimination of HCl: The kinetics of these reactions were investigated at 2-35 Torr total pressure and 265-348 K. The CH₂ClO radical was generated by photolysis of NOCl in the presence of CH₃Cl, O₂, and NO. The CH₂ClO radical reacted with both O₂ and NO, or underwent unimolecular elimination of HCl. The kinetics were determined from growth rates of HC(O)Cl and HCl. The rate coefficient of the CH₂ClO+O₂ reaction was found to be independent of pressure. The temperature dependence can be expressed as: $k(\text{CH}_2\text{ClO} + \text{O}_2) = (2.7 \pm 0.6) \times 10^{-12} \exp[-(646 \pm 128)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate coefficients for the CH₂ClO+NO reaction were found to be independent of both pressure and temperature, with the value $k(\text{CH}_2\text{ClO} + \text{NO}) = (3.0 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate coefficient for unimolecular elimination of HCl from CH₂ClO was found to be pressure dependent, and well into the fall-off. The unimolecular rate coefficient at 8 Torr can be expressed as $(1.4 \pm 0.5) \times 10^8 \exp[-(3700 \pm 140)/T] \text{ s}^{-1}$.

Ab Initio Molecular Orbital and RRKM Calculations of the Unimolecular Dissociation of the CH₂ClO Radical: Ab initio molecular orbital calculations were carried out to study the thermal decomposition of CH₂ClO. The geometries and vibrational frequencies of the reactant, products and transition states for the unimolecular elimination of HCl and Cl from the CH₂ClO radical were calculated at the HF/6-31G(d) and MP2(full)/6-31G(d,p) levels. Total energies were calculated by G2 and G2(MP2) theories. The critical energy for the unimolecular elimination of HCl is predicted to be in the range 8.5 to 9 kcal mol⁻¹ at this level of theory, while Cl-atom dissociation is about 24 kcal mol⁻¹. RRKM calculations were done using moments of inertia, vibrational frequencies and the critical energy from the ab initio computations to predict the rate coefficients of the two unimolecular dissociation channels over a wide range of temperature and pressure. Dissociation to Cl is predicted to be too slow to compete with HCl elimination in the atmosphere. The RRKM rate coefficients agree well with experimental results for the unimolecular elimination of HCl from CH₂ClO with a critical energy of 8.5 kcal mol⁻¹, which is predicted by G2 theory.

A Search for Chemically Activated CH₂ClO Formed in the CH₂ClO₂+NO Reaction: Bilde *et al.* [1999] have published evidence that, in the exothermic reaction of CH₂ClO₂ with NO, chemically activated CH₂ClO is formed, and that a significant fraction of the chemically activated species has sufficient energy to decompose into HCl and HCO. We have initiated experiments designed to look for the decomposition of chemically activated CH₂ClO, and have not been able to verify their result. In our experiments CH₂ClO₂ is formed by photolysis of 33%CH₂ClBr-1%O₂-66%N₂ gas mixtures; in one series of experiments the CH₂ClO radical is formed by the CH₂ClO₂ radical-radical self reaction,



and in a second series of experiments it is formed by reaction with NO.



Reaction (3) is not exothermic enough to form chemically activated CH₂ClO. The CH₂ClO radical will react with O₂, and with NO when it is present, and will also decompose thermally.



Under our conditions these three reactions are observed on a millisecond time scale. If the excited CH₂ClO radical (CH₂ClO*) is formed from the reaction of CH₂ClO₂ with NO, and is followed by reaction (6)



a prompt (< 1 ms) HCl signal should be observed. CH₂ClO decomposition is the only source of HCl in this reaction system, and if it is formed from CH₂ClO* it must be formed rapidly, since by about 1 ms, when we start collecting data, CH₂ClO* will have suffered about 10⁶ collisions and will be completely deactivated. Thus, if reaction (8) is important there would be a significant HCl signal in the first channel of the multichannel analyzer.

Accordingly, the kinetic growth of HCl at $m/z = 36$ was recorded at 284 K and 298 K, at 20 Torr total pressure. Also, the signal intensity of HCl in the first channel, and the background at $m/z = 36$ before and after photolysis experiments were obtained. These experiments were done with both the gas mixture quoted above (NO absent), and with 33%CH₂ClBr-1%O-NO-N₂ gas mixtures. After subtraction of the background from the signal in the first channel no evidence could be found for formation of prompt HCl within an estimated uncertainty of 5%. Thus we estimate that the yield of HCl from reaction 8 is less than 5%.

Thermal Decomposition of the CF₃CFHO Radical: Ab initio molecular orbital calculations were performed to study the thermal decomposition of CF₃CFHO to CF₃ and HC(O)F using the Gaussian 98 series of programs on a Silicon Graphics workstation and on an IBM SP supercomputer. The optimized geometries of the reactant, the products and the transition state were determined at HF/6-31G(d,p) and MP2(full)/6-311G(d,p) levels. The vibration frequencies of the reactant and the transition state were also obtained. The total energies of the reactant, products and transition state were calculated at different levels up to G2(MP2). The barrier height for the thermal decomposition was calculated to be 8.92 kcal/mol at the G2(MP2) level. RRKM calculations were done to predict the rate coefficients of this reaction. The vibrational frequencies and rotational constants were obtained from MP2(full)/6-311G(d,p) optimized geometries. Low and high-pressure limiting rate coefficients were calculated in the temperature range of 250-450 K. For full angular momentum conservation including falloff regime: $k_0(T) = 1.49 \times 10^{-8} e^{-3486/T} \text{ s}^{-1}$, and $k_\infty(T) = 5.67 \times 10^{13} e^{-5015/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The CFCl₂CH₂O Radical: In our experimental investigation of CFCI₂CH₂O, it was found that this radical is stable with respect to unimolecular dissociation for up to 40 ms over the temperature range 251 K to 341 K. It reacts with O₂ instead of decomposing thermally, as does CF₃CFHO and many other halogenated alkoxy radicals. In order to gain better understanding of factors that govern the stability of these alkoxy radicals, a theoretical study of CFCl₂CH₂O was initiated. The HF/6-31G(d,p) and MP(full)/6-311G(d,p) optimized geometries of the ground state, the transition state, and the decomposition products CFCI₂ and CH₂O have recently been completed, and total energy calculations of these species are in progress.

Publications

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Atmospheric Photochemical Kinetics

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Research Objectives

The primary objective of this task is to conduct laboratory studies of stratospheric photochemistry, including absorption cross sections, photolysis quantum yields, product distributions, and reaction rate constants.

Summary of Progress and Results

The relative rate method has been used to measure rate constants for the reactions of OH radical with a series of halocarbons and hydrocarbons. Correlations have been shown between the pre-exponential factors and reaction rates which allow the prediction of an unknown pre-exponential factor from knowledge of the 298 K rate constant. This in turn allows an accurate prediction of the activation energy.

Publications

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Reaction Intermediates and Mechanisms

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Research Objectives

This task is aimed at the elucidation of the kinetics, product distributions, and mechanisms of reactions relevant to stratospheric and tropospheric chemistry. Primary emphasis is placed on processes that function as rate limiting steps in catalytic ozone destruction cycles or that impact the partitioning within chemical families (e.g., ClO_x, BrO_x, FO_x, NO_x and HO_x). Data is obtained using laboratory based chemical reactors. The laboratory techniques employed include discharge flow – mass spectrometry, laser photolysis – laser induced (or resonance) fluorescence and discharge flow – fourier transform spectroscopy.

Summary of Progress and Results

Photolysis Product Yields: Solar photolysis of atmospheric reservoir species is a major source of reactive radicals in the upper troposphere and lower stratosphere. We have succeeded in quantifying the yields of NO₂ and NO₃ from peroxyacetyl nitrate (PAN) and NO₂ from peroxy nitric acid (PNA) at 248 nm. Prior to our experimental determination of PAN quantum yields, photochemical data compilations had considered formation of NO₂ and CH₃C(O)O₂, to be the most likely PAN photochemical process. As a consequence, most tropospheric model calculations to date have assumed a unity quantum yield for NO₂. Our results show that NO₂ is the predominant nitrogen-containing product but not the sole product. A significant amount of NO₃ (\approx 30%) is also produced which impacts the calculated lifetime of PAN and potentially impacts net ozone production in the remote free troposphere.

Photolysis of PNA is also found to involve multiple decomposition pathways. Combining our data on the NO₂ yield with data from a previous study on the OH yield we conclude that the NO₂ and NO₃ producing channels of PNA are of roughly equal importance in the atmosphere.

HO₂ Reactions: The HO₂ radical is a key reactive species in the HO_x family and reactions of HO₂ with BrO and ClO represent rate-limiting steps in catalytic mechanisms of ozone destruction. We have measured rate coefficients for these reactions as a function of temperature and under widely varying reaction conditions. The obtained rate coefficients are significantly smaller at stratospheric temperatures than those measured in previous studies. This will have the effect of slightly lowering the overall catalytic destruction rate of ozone by bromine and chlorine as well as affecting the partitioning of bromine between HOBr and BrO.

We have also investigated possible complex formation in the interaction of H₂O with HO₂. The existence of such a complex has been postulated to explain observations of an enhancement in the rate of the HO₂ self reaction in the presence of water. In our experiments we have observed decreases in HO₂ concentrations in the presence of H₂O that exceed expected losses from the HO₂ self reaction. We ascribe these losses to complex formation and have derived a binding energy for the complex from data taken at several temperatures. The data suggest that significant amounts of the complex will be present in the lower troposphere.

Assessment Activities: The PI has served the NASA Atmospheric Effects of Aviation Project in a number of capacities, including manager of the project's laboratory studies subelement, chairperson for the project's interim assessment and mission scientist for the project's Atmospheric Chemistry of Combustion Emissions Near the Tropopause (ACCENT) aircraft field campaign. He has also served as a coordinating lead author in an international assessment of the effects of aviation on the global environment. The assessment was coordinated by the Intergovernmental Panel on Climate Change in collaboration with the Scientific Assessment Panel to the Montreal Protocol on Substances that Deplete the Ozone Layer.

Publications

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Laboratory Studies of Heterogeneous Processes Related to Stratospheric Ozone Depletion

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Research Objectives

The major objective of this research is to investigate the uptake and reactivity of atmospheric species on sulfuric acid surfaces representative of global stratospheric aerosol. The focus of the current task is on species containing chlorine and bromine. These experiments are performed with the widely-used Knudsen cell reactor technique, developed in our laboratories. Gas phase species are introduced into the upper chamber of a two-chamber reactor and detected by mass spectrometry. A second chamber containing the surface of interest is then opened and the loss of reactant or the production of gas phase products may be ascertained. Gas phase reactions of OH radicals will also be measured. Additionally we are responsible for the data on "three-body" reactions and equilibrium constants that make up Tables 2 and 3, and the notes thereto, of the NASA evaluation of chemical kinetics and photochemistry.

Summary of Progress and Results

We measured diffusion coefficients for HCl and HBr in 30 to 72 wt% sulfuric acid between 220 and 300 K. These experimental results will significantly reduce the error associated with diffusion coefficients used in modeling heterogeneous reactions and in interpreting laboratory data. Diffusion coefficients were measured by using a modified diaphragm cell technique. Among the experimental challenges to making these measurements were: 1) finding a diaphragm material thin enough that the experiments took a reasonable amount of time to complete, and 2) neutralizing the sulfuric acid solution so that the Cl⁻ or Br⁻ ions could be detected with an ion selective electrode, which requires low ionic strength. Our data and formalism are currently used by many other laboratories as an integral part of their data analysis.

SRI International performed laboratory experiments to investigate the solubility and reactivity of acetone in sulfuric acid. Acetone is an important, but only recently recognized, source of HO_x in the upper troposphere, where the heterogeneous loss of acetone may affect its participation in the HO_x and NO_x cycles that control ozone production. The solubility of acetone in sulfuric acid under conditions representative of upper tropospheric and lower stratospheric sulfate aerosol was measured using a low-pressure Knudsen cell reactor. The measured solubility suggests that uptake of acetone by upper tropospheric sulfate aerosol particles is a minor loss process

compared with photolysis. In addition, no reactions of the dissolved acetone were observed for acid compositions below 70 wt% H₂SO₄.

The usefulness of laboratory-measured rates comes from incorporating those rates into models of the atmosphere. Reliable model results depend on reliable rate coefficients. SRI has been involved in the NASA Panel for Data Evaluation for stratospheric chemistry since 1979. Several important reactions for which new experimental data are available were reevaluated for an interim assessment by the NASA Panel.

We have started experiments to investigate the reaction of HOBr + HCl on sulfuric acid surfaces. This reaction becomes important in the stratosphere at low temperatures (<210 K) when a significant amount of HCl is dissolved in the sulfate aerosol: HOBr + HCl → H₂O + BrCl. If this reaction occurs in the atmosphere, production of the easily photolyzed BrCl would provide a mechanism for chlorine activation at temperatures too warm for formation of polar stratospheric clouds. This uptake coefficient has been measured under limited conditions, and further measurements over a wider range of sulfuric acid composition and temperature are called for to reduce the error in the deduced second-order rate coefficient and determine its dependence on atmospheric temperature and water vapor. In addition, because the uptake coefficient is fairly large (~0.2), flow tube measurements may be subject to the gas-phase diffusion limitation, and the Knudsen cell technique can provide a more accurate measurement.

Publications

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Chemical Kinetics of the Stratosphere

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Research Objectives

To use laboratory kinetics and photochemical techniques for the measurement of rate coefficients and product yields of atmospheric reactions. To develop experimental systems for detection of reactive species and for the characterization of aerosol surfaces under atmospheric conditions.

Summary of Progress and Results

Heterogeneous Kinetics: Measurements were made at 296 K of both the forward and reverse reactions: $\text{HNO}_3(\text{g}) + \text{NaBr}(\text{s}) \leftrightarrow \text{HBr}(\text{g}) + \text{NaNO}_3(\text{s})$. The morphologies of the solid phases were studied by using optical microscopy and total surface areas were determined from average granule sizes. After accounting for the interaction of internal diffusion and surface reaction, the uptake coefficients were found to be $(2.8 \pm 0.5) \times 10^{-3}$ and $(1.2 \pm 0.2) \times 10^{-2}$ for the forward and reverse reactions, respectively. The entropy change, ΔS° , obtained from the measured uptake coefficients is -9.17 cal/deg mole; this is in good agreement with the value of -9.08 cal/deg mole obtained from published thermodynamic data.

The interaction of HO_2NO_2 (PNA) vapor with liquid H_2SO_4 was studied at 205-230 K. PNA dissolved in the liquid without undergoing irreversible reaction. The solubility increased with decreasing acid content and decreasing temperature. The heterogeneous reaction between PNA and HCl in liquid H_2SO_4 was found to be very slow ($\gamma < 1 \times 10^{-4}$).

Ice Morphology: Thin ice films formed by deposition from the vapor phase in a fast flow-tube reactor have been characterized *in situ* by using the BET method to determine total surface areas. At 196 K a series of experiments were performed for ice masses ranging from 10.3 to 524.6 mg (thickness = 1.04 to 47.4 μm). The ratio of the total ice surface area to the geometric area was found to vary from 1.6 to 9.3. The specific surface areas were found to vary from $5.92 \text{ m}^2/\text{g}$ for thinner ices to about $0.21 \text{ m}^2/\text{g}$ for thicker ices; these values are in good agreement with previous results obtained for thicker ice films in a separate apparatus. Ice films were further characterized by using environmental scanning electron microscopy to obtain particle sizes and shapes, and to investigate the morphology of the ices prepared under conditions similar to those used in the

flow-tube experiments. The electron micrographs clearly show that these ice films are comprised of almost uniformly sized granules stacked in layers and that the average granule size increases with deposition time and, hence, with thickness.

Reaction of Cl + CH₄: Absolute rate data for the Cl(²P₁) + CH₄ → HCl + CH₃ reaction have been obtained from 218 to 298 K by using the discharge-flow resonance fluorescence technique in helium at 1 Torr total pressure. The result at 298 K is $(10.1 \pm 0.6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The temperature dependence in Arrhenius form is $(6.5 \pm 0.9) \times 10^{-12} \exp[(-1235 \pm 34)/T]$. The errors given are one standard deviation; overall experimental error is estimated at $\pm 15\%$. Because of the relatively large disagreement among earlier measurements at low temperatures, the results were examined for possible effects of non-Boltzmann spin distribution and vibrational excitation of CH₄, secondary chemistry of CH₃ radicals, and impurities in the Cl atom and CH₄ sources. There was no significant change in the observed rate constant when an efficient spin quencher, CF₄, was added and estimates indicate that vibrational partitioning in CH₄ should be at the ambient reactor temperature before the start of the reaction. The results were also independent of the source of Cl atoms (microwave discharge or thermal decomposition of Cl₂) and whether CH₄ was purified *in situ*. However, the observed rate constant did depend on initial Cl atom concentrations and to a lesser extent on CH₄ concentrations. Numerical simulations were used to assess the importance of secondary chemistry over a range of reactant concentrations.

Publications

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Photochemical and Kinetic Measurements of Stratospheric and Tropospheric Importance

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Research Objectives

This task focuses on the elucidation of atmospheric photochemical and kinetic processes through laboratory studies of select chemical systems. Experiments are designed and conducted to determine the temperature and pressure dependencies of rate constants and to infer the mechanisms for those processes important in the modeling of atmospheric chemistry. Photochemical parameters are also determined to assist in the kinetic measurements or aid in the interpretation of the data, or as direct input for the determination of atmospheric properties. While the research emphasis is directed towards an assessment of the effects of anthropogenic activity on stratospheric chemical composition, certain predominantly tropospheric reaction systems are often investigated because of their influence on chemical transport to the stratosphere and/or their mechanistic similarities to stratospheric processes. In particular, the kinetic and photochemical parameters are used to calculate the atmospheric lifetimes of various ozone and climate related source gases and thence their ozone depletion potentials and/or global warming potentials. Finally, ab initio calculations are conducted on various reaction systems to determine the suitability of certain calculational methods for predicting chemical reactivity and thereby for serving as screening tools for estimating atmospheric lifetimes and environmental properties.

Under this task, the principal investigator also serves as a member of the NASA Panel for Data Evaluation and assists in the periodic preparation of a tabulation of evaluated kinetic and photochemical data applicable to atmospheric modeling. He also provides advisory services to the Upper Atmosphere Research Program (UARP) of NASA's Office of Earth Science (regarding the direction, evaluation, and review of the major program elements) and serves as Program Scientist for various UARP field measurement experiments using aircraft-borne, balloon-borne, and ground-based instrumentation. Finally, the PI participates as an author and reviewer in various national and international assessment activities relating to atmospheric chemistry in general and stratospheric ozone in particular.

Summary of Progress and Results

Laboratory activities under this task during the period 1997 through 1999 were primarily in the category of hydroxyl radical kinetic investigations performed using the flash photolysis resonance fluorescence (FPRF) technique. Accomplishments include the measurements of the temperature dependencies of the rate constants for the reactions of OH radicals with a variety of naturally occurring and anthropogenic halocarbons. Studies have included: CH₂Cl₂, CH₃CF₂CF₃ (HFC-245cb), CH₂CHCF₃, CH₂CFCF₃, CF₂CFCF₃, CF₂CF₂, CHF₂OCHF₂ (HFOC-134), and CF₃CH₂OCH₂CF₃ (HFOC-356mff). The rate constant results thus obtained were used in a comparative kinetic analysis with those for methyl chloroform to determine approximate tropospheric lifetimes of the compounds. For several compounds, measurements were also made of the UV spectra, whereas for others the infrared cross-sections were measured for use in estimating global warming potentials.

Ab initio calculations were performed for the hydrogen atom abstraction reactions (by OH) from a series of halogenated methanes. Calculations were performed at various levels of theory for a variety of basis sets in an effort to determine the suitability of the different levels for reproducing experimental results in a calculationally efficient manner. These methods are being extended to a variety of other naturally occurring and anthropogenic trace gases to examine their utility as forecast tools for atmospheric reactivity.

During the three-year period covered by this report, the PI participated in the preparation and review of the 12th Evaluation of Photochemical and Kinetic Data for Use in Stratospheric Modeling by the NASA Panel for Data Evaluation. He also served as a lead author of a chapter on short-lived ozone related source gases in the 1998 international Scientific Assessment of Ozone Depletion. This assessment was coordinated by the World Meteorological Organization and the United Nations Environment Programme as prescribed under the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer. The PI also served as a technical reviewer for several other chapters in the Assessment.

Finally, the PI served as Program Scientist for the 1995-1997 Stratospheric Tracers of Atmospheric Transport (STRAT) airborne experiment conducted from Moffett Field, California and Barbers Point, Hawaii; for the 1997 Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) airborne campaign conducted from Moffett Field, California and Fairbanks, Alaska; and for the Observations from the Middle Stratosphere (OMS) balloon campaigns associated with these airborne experiments and conducted from bases at high, mid-, and tropical latitudes.

More detailed information on all of the activities that have been described above may be found in the following publications.

Publications

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Homogeneous and Heterogeneous Processes of Atmospheric Interest

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Research Objectives

The primary objective of this task is to obtain direct laboratory measurements of kinetic rate parameters for homogeneous and heterogeneous reactions important in stratospheric chemistry, and to develop new experimental techniques for the laboratory study of polar ozone chemistry.

Summary of Progress and Results

Laboratory activities under this task during 1997 and 1998 primarily concern the heterogeneous chemistry on the surface of atmospheric aerosols. Accomplishments include:

- *Morphology and Surface Areas of Thin Ice Films:* In the present study, ice films are formed in such a reactor and their surface areas are determined *in situ* from BET (Brunauer, Emmett, and Teller) analysis of gas adsorption isotherms. The measured surface areas are found to be strongly dependent on the total mass of ice deposited. The specific surface areas of ices prepared at 77 K or 196 K are consistent with previous data obtained by using thicker nonuniform ice films. In a separate apparatus, environmental scanning electron microscopy (ESEM) is used to obtain particle sizes and shapes, and to investigate the morphology of the ices prepared on borosilicate, aluminum and silicon substrates. Ice films on borosilicate substrates are found to comprise micron-sized granules randomly packed in layers. The uptake of HCl in ice films prepared at 196 K using the same flow-tube reactor is also measured to be approximately 1×10^{14} molecules/cm² when a partial pressure of HCl about 5×10^{-7} Torr is used. Similar to the surface areas, the total uptake is strongly proportional to the mass of ice deposited. The combined evidence suggests that even for thin ice films: (1) surface areas are greater than the geometric area of the flow-tube reactor; and (2) interaction of pore diffusion with surface reaction should account for in the determination of uptake and heterogeneous reaction rates.
- *Heterogeneous Interaction of Peroxyacetyl Nitrate with Liquid Sulfuric Acid:* The uptake of peroxyacetyl nitrate (PAN) on liquid sulfuric acid surfaces has been investigated using a fast-

flow reactor coupled to a chemical ionization mass spectrometer. PAN was observed to be reversibly adsorbed on sulfuric acid. From the time-dependent uptake, Henry's law solubility constant of PAN in sulfuric acid was obtained. The measured solubility constant was found to depend strongly on temperature (199–226 K), but weakly on acid composition (46–72 wt%). On 72 wt % H₂SO₄, for example, the effective Henry's law solubility constant was determined to be about 5.6×10^4 and 3.1×10^3 M/atm at 208 and 222 K, respectively. Heterogeneous reactions of PAN with HCl, Cl, ClO, and OCIO on liquid sulfuric acid was also investigated and found to be very slow ($\gamma < 0.0001$).

- *Quantitative Analysis of the Infrared Absorptivities of Nitric Acid Ices Existing in Polar Stratospheric Clouds:* The infrared absorptivities of nitric acid ices formed vapors containing water and nitric acid were investigated by means of a Fourier-transform infrared spectrometer operated at a wavelength resolution of 1.0 cm⁻¹. The solid films were prepared on the surface of a gold-coated, polished copper plate at a temperature of 153 to 198 K. After collecting the infrared spectra, the substrates were vaporized and condensed into a U-tube for quantitative analyses of H₂O and HNO₃, using a quadrupole mass spectrometer. Amorphous forms of nitric acid ices and four crystalline hydrates (NAM, NAD, α -NAT, and β -NAT) were identified and their infrared absorptivities measured. The infrared spectra were interpreted in terms of the known spectra of oxonium and nitrate ions. Possible implications for remote sensing and analysis of polar stratospheric clouds using these spectra are discussed.
- *Kinetics of the Heterogeneous Reaction HNO₃(g) + NaBr(s) → HBr(g) + NaNO₃(s):* The kinetics of the heterogeneous reaction HNO₃(g) + NaBr(s) → HBr(g) + NaNO₃(s) has been investigated at 296 K using a fast-flow reactor coupled to an electron-impact ionization mass spectrometer. The results indicate that the uptake process comprises both physical adsorption and chemical reaction. The uptake coefficients for the forward and reverse processes, after accounting for internal surfaces by means of a mathematical model of surface reaction and pore diffusion, were found to be $(2.8 \pm 0.5) \times 10^{-3}$ and $(1.2 \pm 0.2) \times 10^{-2}$ at 296 K, respectively. The implications for atmospheric chemistry in the marine boundary layer and Arctic troposphere are discussed.
- *Uptake of Acetone in Liquid Sulfuric Acid:* The uptake of acetone by liquid sulfuric acid has been investigated over the range of 40–80 weight % H₂SO₄ and between the temperatures of 198 to 300 K. Studies were performed with a flow tube reactor and used a quadrupole mass spectrometer for detection. At most concentrations studied, acetone was physically absorbed by sulfuric acid without undergoing irreversible reaction. However, at acid concentrations at or above 80 weight %, reactive uptake of acetone has been observed, leading to condensation products such as mesityl oxide. From time dependent uptake data and diffusion coefficients calculated from molecular viscosity, the effective Henry's Law solubility constant (H*) was determined. The solubility of acetone in liquid sulfuric acid was found to increase with increasing acid concentration and decreasing temperature. In the 75 weight % and 220 K range, the value for H* was found to be 3.7×10^6 M/atm. This value suggests that at quiet tropospheric conditions, the majority of acetone will be found in the gas phase rather than absorbed by atmospheric sulfate.
- *Solubilities of PAN and PNA in Water and Liquid Sulfuric Acid:* We analyze literature values of the Henry's law constants of peroxyacetyl nitrate (CH₃C(O)O₂NO₂, PAN) and peroxynitric acid (HO₂NO₂) in water and liquid sulfuric acid, and derive correlative expressions to predict

the solubilities of PAN and HO₂NO₂ in liquid H₂SO₄ over a wide range of temperature and acidic composition. To a first-order approximation, the results indicate that the Henry's law constants (in units of mol kg⁻¹ atm⁻¹) are ln(H) = 1.07 - mH₂SO₄ × (0.69 - 152/T) - 5810 × (1/T₀ - 1/T) for PAN and ln(H) = 3.69 - mH₂SO₄ × (- 0.25 + 65/T) - 8400 × (1/T₀ - 1/T) for HO₂NO₂ where mH₂SO₄ is the molality of sulfuric acid, T is the temperature of solutions, and T₀ = 298.15 K. The activity coefficients of PAN and HO₂NO₂ in aqueous H₂SO₄ are found to have a simple relationship with the molality of H₂SO₄.

- *Uptake of Nitric Acid Vapor by Soot:* The uptake and decomposition of HNO₃ on black carbon (soot) surfaces were investigated in order to evaluate the proposal that HNO₃ decomposition on aircraft-generated soot aerosols may alter the NO_x/NO_y partitioning in the upper troposphere and lower stratosphere. Black carbon samples used as surrogate material for aircraft soot in this study included Degussa FW2 (an amorphous carbon black comprising medium oxides), graphite, hexane soot, and kerosene soot. The measurements of uptake were performed by varying P(HNO₃) in the range of 5 × 10⁻⁷ ~ 5 × 10⁻⁴ Torr at 220 K and 295 K. The present results suggest that the HNO₃ decomposition on soot aerosols through a direct gas-solid interaction, which was proposed as a possible NO_y-reactivation mechanism in the atmospheric modeling, should be dismissed.

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Laboratory Studies of the Infrared Optical Constants and Microphysical Properties of Stratospheric Aerosols

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Research Objectives

In recent years, it has become apparent that stratospheric aerosols dramatically impact a wide array of atmospheric processes. Unfortunately, our level of understanding of these effects are still quite primitive, in comparison to the effects of gas-phase species. Progress is being made quite rapidly, due to the combined efforts of field measurements, laboratory studies, and atmospheric modeling. There is, however, a need to develop new approaches for performing detailed studies on the formation of stratospheric aerosol species, as well as the characterization of their properties under conditions that mimic those found in the stratosphere. We have previously reported a method for obtaining frequency-dependent optical constants directly from the infrared extinction spectra of laboratory-generated aerosols. During the most recent grant period, we have developed a new instrumental approach employing *in situ* high resolution laser spectroscopy for characterizing our experimental conditions with unprecedented accuracy. Specifically, measurements of equilibrium vapor pressures within a new flow cell provide quantitative information of the composition and phase of the volatile aerosols. Using this new approach, we have expanded the database of available aerosol optical constants, and have begun to explore aerosol phase transitions, under relevant stratospheric conditions.

Summary of Progress and Results

We constructed a new and innovative flow cell apparatus for producing and spectroscopically characterizing cryogenic aerosols. The cell is a U-shaped tube comprised of six independently cooled regions, each having an operating range of $120 - 300 \pm 1$ K. The geometry allows aerosols to be formed and observed at different temperatures, a feature that is important since the temperature in the nucleation region largely controls the particle size, a property of the aerosols we need to vary independent of the observation temperature. In the experiments performed to date, the vapors of interest flow into the top of the cell in a carrier gas of helium or nitrogen, where they are cooled by the first section of the cell and become supersaturated, forming aerosols by homogeneous nucleation. For sulfuric acid, the aerosols were formed using a

vaporizer outside of the cell. The final aerosol composition was achieved in all experiments by adjusting the relative flows of acid and water vapors into the cell. Broad band FT-IR extinction spectra were recorded to provide information on the optical constants and phase of the aerosols.

Aerosol compositions were determined *in situ* using a high resolution infrared tunable diode laser to accurately measure the vapor pressures of the relevant vapor-phase species in the cell. Assuming the aerosols are in equilibrium (a condition we have tested extensively), their composition can be determined through Henry's Law [Carslaw *et al.*, 1995]. The development of this system was facilitated by the collaboration we have established with Douglas Worsnop at Aerodyne Research, Inc. We have developed a method for determining complex refractive indices directly from aerosol extinction spectra, which is discussed in detail elsewhere [Niedziela *et al.*, 1998]. Our method has been tested extensively, and it converges well to results that agree with literature values, where available. The final data sets we obtain are rather large, and we have thus chosen to make them available on an internet-accessible site where researchers can download the complete files by anonymous FTP. These data sets have been retrieved by a number of satellite data analysis and climate modeling groups, who are now using them in their applications.

Our earlier studies had focused on the crystalline hydrates of nitric acid, since the infrared spectra of these aerosols are sufficiently characteristic to provide unique composition determinations without the need of a diode laser system. The tunable diode laser system became important when the spectra of the aerosols were insufficient for composition determinations, as in the case of liquid sulfuric acid. As a result of our extensive study of this important aerosol system, we have determined the optical constants from 200 – 300 K over a wide range of atmospherically relevant compositions. Significant changes were observed in the data collected at stratospheric temperatures when compared with the room temperature results of Palmer and Williams [1975]. These changes are due to a combination of the shift in ionic equilibrium with temperature and the effects this has on the hydrogen bonding network. We performed a similar but less extensive study on supercooled liquid nitric acid aerosols, which show similar temperature-dependent changes. From this work we concluded that supercooled nitric acid aerosols could not be modeled accurately using amorphous solid optical constants [Toon *et al.*, 1994]. These studies of the nitric acid binary aerosols enabled us to test our diode laser system for probing more than one vapor-phase species, specifically water and nitric acid. This is essential for our ongoing studies of ternary and organic-containing aerosols.

We have made considerable progress in studies of aerosol microphysics. In particular, we have studied the melting of crystalline NAD and the freezing of aerosols of 63 weight % nitric acid. This has enabled us to explore the associated phase boundaries and to estimate the freezing rates in this system. These exploratory experiments are aimed at establishing a combination of techniques for future studies of the microphysical and chemical properties of the atmospheric aerosol particles, such as phase transitions and chemical uptakes. The nucleation rates obtained from this experiment are in qualitative agreement with those of Bertram and Sloan [1998], although the present rates are nearly an order of magnitude higher. Our experiments benefit tremendously from the more accurately determined optical constants of liquid nitric acid at low temperatures, which allows better estimate of aerosol size distributions. Our unique ability to determine liquid composition *in situ* eliminates the associated uncertainties.

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Flow Tube Studies of Gas Phase Chemical Processes of Atmospheric Importance

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Research Objectives

This task is aimed at the laboratory characterization of chemical processes which are potentially important in connection with stratospheric ozone depletion. The investigations involve measurements of elementary rate constants and photochemical parameters of homogeneous gas phase reactions over pressure and temperature ranges that cover stratospheric conditions. The systems under study include reactions of the OH, ClO, HO₂ and NO₂ radicals.

Summary of Progress and Results

The branching ratio for the OH + ClO reaction has been measured using the turbulent flow technique with high-pressure chemical ionization mass spectrometry for the detection of reactants and products. In our earlier study, OD was used instead of OH due to the large HCl background produced by the ClO source. Improvements to our experimental technique have significantly reduced this HCl background, thus making it possible to observe directly the production of very small concentrations of HCl ($\sim 10^9$ molecule cm⁻³) from the minor channel of the OH + ClO reaction. At room temperature and ~100 Torr pressure, the rate constant for this minor channel was determined to be $(9.5 \pm 1.6) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ with a two standard deviation error limit, which remained unchanged when the pressure was increased to 200 Torr. The temperature dependence of the rate constant for this minor channel was also investigated between 207 and 298 K, and the data was fit to the following Arrhenius expression: $(3.2 \pm 0.8) \times 10^{-13} \exp [(325 \pm 60) / T]$ cm³ molecule⁻¹ s⁻¹. The branching ratio for the HCl channel was determined to be 0.07 ± 0.03 at all pressures and temperatures investigated in this study. Statistical rate theory calculations were also performed on the OH + ClO reaction system and are in good agreement with the experimental results.

Using the same turbulent flow – chemical ionization mass spectrometry technique, the elementary rate constant for the ClO + NO₂ + M reaction was measured between 150 and 600 Torr, at 298 K and at 213 K. This work represents the only experimental measurement to date of this rate coefficient at temperatures below 248 K. The results are in excellent agreement with the values recommended by the NASA Panel for Data Evaluation.

The quantum yields in the photolysis of dichlorine monoxide, Cl_2O , have been determined at 320, 360, 400, and 440 nm, at a total pressure of 50 Torr. The technique employed involved a slow-flow tubular photolysis reactor fitted with a chemical ionization mass spectrometer detector for measurements of trace species produced in the photolysis. The light source consisted of a xenon arc lamp attached to a monochromator. The results indicate unit quantum yield at all the wavelengths under investigation, in disagreement with some earlier literature reports.

The quantum yields for the production of electronically-excited oxygen atoms, $\text{O}(\text{'D})$, in the photolysis of ozone in the wavelength range from 290 to 350 nm have been investigated using the slow-flow technique with chemical ionization- mass spectrometer detection of the photolysis products. The $\text{O}(\text{'D})$ atoms were monitored indirectly after conversion to NO_2 by sequential reactions with N_2O and O_3 . The results indicate a quantum yield of about 0.2 around 315 to 320 nm, and 0.1 around 325 to 330 nm. These results support recent laboratory work indicating that a spin-forbidden channel is active at these longer wavelengths, yielding quantum yields significantly greater than zero.

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Molecular Beam Studies of Stratospheric Photochemistry

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Research Objectives

The photochemistry of chlorine peroxide, ClOOCl, is central to the most important of the catalytic cycles which lead to the destruction of stratospheric ozone under the highly perturbed conditions found above the poles during Polar winter and early spring. The efficiency of this catalytic cycle is directly proportional to the chlorine atom yield from cleavage of the Cl-O bond when ClOOCl absorbs UV light. Dissociation of the peroxy O-O bond would lead to ClO and a null catalytic cycle. The goal of this task in 1997 and 1998 was to perform a laboratory determination of the branching ratio between Cl and ClO upon photolysis of ClOOCl at 248 and 308 nm using mass spectrometric detection in a molecular beam photodissociation apparatus. The technique, photofragment translational spectroscopy, allows for direct detection of primary photoproducts in the absence of interfering secondary chemistry. The direction of this task changed in 1999, to a three year study requiring the development of an infrared cavity ringdown spectrometer for laboratory studies of the HCl yield from the reaction of OH + ClO, a process which influences model predictions of stratospheric ozone at mid-latitudes.

Summary of Progress and Results

Laboratory Study of Photodissociation of ClOOCl at 248 and 308 nm: Investigations on the photodissociation of ClOOCl at 248 and 308 nm were performed using photofragment translational spectroscopy, with mass spectrometric detection of products using the Crossed Molecular Beams Apparatus originally located at Jet Propulsion Laboratory and moved during the course of these experiments to Montana State University. All experiments were completed, and a preliminary communication was submitted in 1998 and published in 1999.

Time-of-flight and angular distributions of all observed products were collected in order to determine the primary and secondary photolysis channels and their relative yields. At 248 nm, Cl, ClO, and O₂ products were observed from the photodissociation of ClOOCl (after subtracting out signal arising from Cl₂O photolysis). Both ClO and Cl products were produced from multiple competing channels. At 308 nm, the data was more difficult to interpret because of

extensive interference from Cl₂ and Cl₂O byproducts, but there was evidence for both Cl and ClO products from ClOOCl photolysis. The key to the success of this experiment was the development of an intense ClOOCl beam source. Extensive analysis was required, because of the presence of many precursors and byproducts in the beam. Detailed studies of dichlorine monoxide photolysis, Cl₂O, were also performed and published.

Our best estimates of the Cl:ClO branching ratios are 0.88:0.12 and 0.90:0.10 at 248 nm and at 308 nm, respectively. The upper limit for the relative yield for ClO products is 31% at 308 nm and 19% at 248 nm. These values are somewhat lower than a previous laboratory measurement at 308 nm of Molina *et al.*, but the new results substantially support current models of ozone loss in the Arctic and Antarctic spring which assume significant ozone loss through ClOOCl-related catalytic cycles.

Cavity Ringdown Apparatus for Free Radical Kinetics: During 1998 and 1999, development was begun on an apparatus for laboratory measurements of free radical kinetics employing infrared cavity ringdown detection for ultrahigh sensitivity detection of molecules in the 3 micron spectral region. A high power, pulsed infrared laser source using optical parametric amplification has been built and tested, and cavity ringdown detection has been successfully achieved. Current efforts focus on testing the limits of sensitivity for HCl, and on fabrication of a IR Kinetic Spectroscopy apparatus for performing the kinetics measurements of the reaction OH + ClO. This task is being performed in collaboration with the Chemical Kinetics and Photochemistry Group at the Jet Propulsion Laboratory.

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Laboratory Studies of Reactions and Photochemistry of Halogenated Species That Affect Stratospheric Ozone Abundance

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Research Objectives

This project involves the application of spectroscopy to the study of rates, intermediates and products of reactions that are important in the Earth's stratosphere. The experiments are carried out using a high resolution Fourier transform spectrometer, a linear photodiode array spectrometer, and a monochromator to obtain IR, visible, and UV spectra of transient and stable species of atmospheric importance. Reaction rate coefficients, absorption cross sections, and reaction mechanisms are investigated. The obtained data helps to improve our knowledge of stratospheric chemistry, to understand the extent and rates of ozone level changes, and to provide spectroscopic data for laboratory and field measurements.

Summary of Progress and Results

Gas Phase Photochemistry of Halogen Reservoir Species: (a) The quantum yields for the production of Cl, O, ClO and NO₃ in the photolysis of ClONO₂ were measured by detecting Cl and O atoms by atomic resonance fluorescence and NO₃ by long path laser absorption. It is concluded that Cl and NO₃ are the major products in the photolysis of ClONO₂ at wavelengths important in the stratosphere and that the total quantum yield for dissociation is close to 1. (b) Quantum yields for NO₃ production in the photolysis of BrONO₂ were and found to be independent of pressure over the range 150 to 600 Torr and bath gas (N₂ or O₂). Yields of other products such as Br and BrO were also estimated. The measured values for NO₃ production in the photolysis of N₂O₅ were 0.64, 0.96, and 1.03 at 248, 308, and 352.5 nm respectively. The absorption cross sections for N₂O₅ between 208 and 398 nm were also determined.

Based on our measured photochemical data, the role of chlorine and bromine in determining the stratospheric ozone abundance is better defined.

Reactions of Halogen Species: (a) The rate coefficient for the reaction O(³P) with ClONO₂ was measured between 202 and 325 K to be $k = 4.5 \times 10^{-12} \exp(-900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It was shown that ClO and NO₃ radical are the major products in this reaction. (b) In collaboration with NCAR, the gas phase reactions BrONO₂ and ClONO₂ + O₃ → products were examined at 235 K and 700 Torr N₂. The loss of BrONO₂ and ClONO₂ were measured to be independent of the O₃ concentration yielding upper limits of $< 1 \times 10^{-20}$ and $< 4 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively,

for the rate coefficients for these reactions. (c) The rate coefficient for the reaction $\text{OH} + \text{ClO} \rightarrow$ products was measured to be $k(T) = 8.9 \times 10^{-12} \exp(295/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. (d) Rate coefficients for the reactions $\text{Br} + \text{BrONO}_2 \rightarrow \text{Br}_2 + \text{NO}_3$ and $\text{Cl} + \text{BrONO}_2 \rightarrow \text{ClBr} + \text{NO}_3$ were measured at 298 K to be 6.7×10^{-11} and $1.27 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The NO_3 product yields for the reactions were measured to be 0.88 and 1.04, respectively.

These studies placed the role of halogens in the stratosphere on a firmer footing by quantifying the rates of above reactions.

Gas Phase Studies of NO_x Chemistry: (a) The rate coefficient for the reaction of $\text{O}(\text{P}^3)$ atoms with NO_2 , the rate limiting step in the major catalytic ozone destruction cycle involving NO_x , was very accurately measured to be $k(T) = 5.26 \times 10^{-12} \exp(209/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-412 K. (b) Using a two-dimensional model, the revisions in the rate coefficients for the $\text{O} + \text{NO}_2$, $\text{OH} + \text{HNO}_3$, and $\text{OH} + \text{NO}_2$ reactions were shown to increase calculated NO_x abundance (up to 40%) and NO_x -catalyzed O_3 destruction, and extend down by several kilometers the altitude region where NO_x dominates, and reduced by approximately 30% the model derived long-term O_3 trend at midlatitudes due to increases in anthropogenic halogens. (c) It was shown that the model derived NO_x to HNO_3 ratio agrees substantially better with observations when newly measured rate coefficients for the $\text{OH} + \text{NO}_2$ and $\text{OH} + \text{HNO}_3$ reactions are used. The ozone changes associated with the emissions of a fleet of supersonic aircraft were also shown to be altered.

The information from these studies have significantly revised our understanding of the role of NO_x in ozone destruction cycles and shown that nitrogen oxides are more important over a wider altitude range in determining stratospheric ozone levels.

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Laboratory Studies of Tropospheric and Stratospheric Reactions

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Research Objectives

The primary objective of this task is to study the rates and mechanisms of key elementary gas-phase reactions important in stratospheric and tropospheric chemistry. A secondary objective is to utilize high resolution spectroscopic methods in the ultraviolet, infrared and microwave regions to obtain structural and spectroscopic information concerning atmospheric molecules.

Summary of Progress and Results

Our work has focused on improving and extending our understanding of gas-phase photochemical and kinetic mechanisms important in stratospheric ozone depletion. The specific areas of research include the following:

Gas-Phase Reaction Kinetics Studies: The ClO + HO₂ reaction is a key process in the catalytic destruction of ozone in the lower stratosphere. Despite this reaction's important role there has been only one previous temperature dependence study. This study, published in 1979, obtained a highly nonlinear Arrhenius dependence with essentially no temperature dependence above room temperature and an E/R of -700 below room temperature. We have now completed two extensive experimental and theoretical studies of this reaction, one by flash photolysis/UV absorption and one by discharge flow/mass spectrometry. The FP/UV study covered the temperature range 203-364 K and pressure range 50-700 Torr while the DF/MS study spanned the temperature range 233-380 K at a pressure of 1 Torr. The difference in the results between our two studies has been analyzed extensively. *Ab initio* calculations have shown that there are a number of stable HClO₃ isomers that may be metastable or stable on the HO₂ + ClO potential surface. In collaboration with the group of Professor J. S. Francisco at Purdue University, the first calculations have been performed on the energetics of the transition states that connect HClO₃ intermediates with their product decomposition products, i.e., HOCl + O₂ and HCl + O₃. The results indicate that the HOOCl intermediate is strongly bound and that the barrier towards decomposition is large.

Kinetics studies have been carried out on the reactions of organic peroxy radicals (RO_2) with hydroperoxyl radicals (HO_2). This class of reactions is important in the cleanest parts of the troposphere such as the marine boundary layer and remote high latitude regions that have very low NO_x concentrations. A new apparatus has been developed to study these reactions which overcomes some of the problems inherent in previous approaches. The new apparatus uses excimer laser photolysis to initiate the kinetics, and two separate absorption probes to monitor HO_2 and RO_2 . HO_2 radicals are probed using a long-path RF-modulated distributed feedback (DFB) laser at 1.41 microns, while the HO_2 radicals are probed using a deuterium lamp. This system has been used to study the $\text{HO}_2 + \text{HO}_2$ and $\text{HO}_2 + \text{CH}_3\text{CH}_2\text{O}_2$ reactions at room temperature. This work is carried out in collaboration with the group of Professor Mitchio Okumura at Caltech.

Photodissociation and Spectroscopic Studies: In a collaboration with the group of Professor Paul Wennberg at Caltech we have used the optical train of our FP/UV apparatus to measure band strengths for overtones of several atmospheric molecules including HO_2NO_2 , H_2O_2 and HNO_3 . This work was stimulated by the inability of atmospheric models to predict successfully the diurnal variation of OH and HO_2 from high latitude flights of the ER-2 during POLARIS. The band strengths of the three molecules were measured using a two-color technique. The near-IR spectra were calibrated relative to well-known cross sections in the UV at 250 and 260 nm. In this way, band strengths for both $3\nu_{\text{OH}}$ and $4\nu_{\text{OH}}$ were measured for all three molecules. Previously only the band strengths for HNO_3 had been determined.

Photodissociation studies have been carried out on peroxyacetyl nitrate (PAN) and peroxynitric acid (PNA), two important temporary reservoirs of NO_x in the troposphere and stratosphere. Photodissociation of these molecules was carried out at 248 nm, and the quantum yields for NO_2 and NO_3 production were measured using the technique of laser-induced fluorescence (LIF). The results indicated that both the NO_2 and NO_3 channels were important at 248 nm.

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Reaction Rate and Reaction Product Measurements**Principal Investigator:** Louis J. Stief

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Research Objectives

Reaction rate constants for atmospheric reactions are measured and primary reaction products identified and quantitatively measured, both in as direct a manner as possible. Recent research has emphasized the reactions of halogen oxide radicals with atomic oxygen and reactions of halogen-substituted hydrocarbon radicals with molecular oxygen. Supporting photoionization mass spectrometry (PIMS) studies at the National Synchrotron Light source, Brookhaven National Laboratory (BNL), provide spectroscopic and thermodynamic data for species such as XO, HOX, X₂O and OXO.

Summary of Progress and Results

We have measured the rate constant for the atom-radical reaction O + IO in a low pressure discharge flow-mass spectrometry (DF-MS) system with [OI] in large excess and accurately determined in separate titration experiments. These conditions minimized contributions to the IO loss rate from secondary reactions. A one parameter fitting to a numerical model gives $k(O+IO) = (1.5 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at T = 298 K. Attempts to measure k(O+IO) at T = 225 K were frustrated by complete loss of IO signal.

In collaboration with Vladimir Orkin of the National Institutes of Standards and Technology (NIST), Denis Bogan, and Walter Payne have examined the yield of the olefin product for the reaction of halogen-substituted C₂-hydrocarbon free radicals with O₂. Such radicals are formed in the atmosphere by the reaction of OH with halogen-substituted C₂-hydrocarbon molecules. In the case of CF₂HCF₂H (HFC-134), the yield of the olefin C₂F₄ is < 0.1 % at P = 1 Torr He and T = 298 K. For comparison, it has previously been observed that for the analogous C₂H₅ + O₂ reaction, the yield of C₂H₄ is ≈ 30 % under these same conditions. In seeking to elucidate the effect of halogen identity and degree of substitution on the olefin yield, we have investigated the reactions of O₂ with C₂H₄Cl and C₂H₄Br at T = 298 K and P = 0.4 to 2.0 Torr He. The yield of C₂H₃Cl is in the range 2 to 5 % and the corresponding rate constants for C₂H₄Cl + O₂ → C₂H₃Cl

+ HO₂ are $(1.7 \pm 0.8) \times 10^{-14}$ at P = 0.4 Torr and $(4.1 \pm 1.3) \times 10^{-14}$ at P = 2.0 Torr, both in units cm³ molecule⁻¹ s⁻¹. Studies of the formation of C₂H₃Br from the reaction C₂H₄Br + O₂ are underway.

Using a DF-PIMS apparatus with dispersed synchrotron radiation as the ionizing source, we have collaborated with Bruce Klemm and his associates (BNL) and with Thomas Buckley and Russell Johnson (NIST) on measurements of the photoionization spectra, ionization energies and heats of formation of free radical and metastable molecular species of atmospheric interest: IE(HOCl) = 11.12 eV, the first photoionization study; IE(OBrO) = 10.29 eV, the first experimental measurement; an ab initio calculation yields IE = 10.26 eV in excellent agreement with the experimental result; ΔH_f(HOCl) = 18.3 kcal mol⁻¹ from our measured ΔH_f(Cl₂O) and a published value for K_{eq}(Cl₂O + H₂O ↔ 2 HOCl). From measurements of the appearance energy for the formation of BrO⁺ from OBrO, we will derive the first experimental measurement of ΔH_f(OBrO). An ab initio calculation is also in progress. These data are essential in evaluating the thermochemistry of potentially significant atmospheric reactions involving these species.

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Reactions of the Upper Troposphere and Lower Stratosphere

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Research Objectives

The goal of this research project was to quantify the rates and mechanisms of some gas-phase chemical reactions of importance to the chemistry of the upper troposphere and lower stratosphere. Studies of the upper tropospheric chemistry were focused on the oxidation mechanisms of organic species, which may be present due to convection from lower altitudes, and whose oxidation (in the presence of NO_x) provides a source of ozone. Studies of relevance to the lower stratosphere were centered around the chemistry of chlorine and bromine species and their effects on stratospheric ozone levels.

Summary of Progress and Results

The oxidation mechanism for a series of organic species (ethene, propene, cyclohexane, cyclopentane) have been studied at temperatures relevant to the entire troposphere, using environmental chamber/FTIR techniques. The end products observed (mostly aldehydes and ketones) were interpreted in terms of the chemistry of the alkoxy radicals formed in the oxidation. In general, the A-factors and the activation barriers for carbon-carbon bond rupture in the alkoxy radicals are both shown to be considerably lower than previously believed. In addition, chemical activation effects are shown to be important in the oxidation of the alkenes. That is, β-hydroxyalkoxy radicals, formed in the exothermic reaction of the corresponding peroxy radical with NO, are energized such that significant fractions (25% in the case of ethene and 75% in the case of propene) undergo prompt (sub-nanosecond) decomposition before collisional thermalization can occur. As a result, larger yields of decomposition products (e.g., formaldehyde from ethene) are obtained under conditions relevant to the upper troposphere than previously believed.

Rate coefficients for the reaction of Cl-atoms with CH₃Cl, CH₂Cl₂, and CHCl₃ have been determined as a function of temperature. Noteworthy was the finding that the reactions of Cl with CH₂Cl₂ and CHCl₃ are both 1.5-2 times faster than previously believed at 220 K.

Mechanisms for the atmospheric oxidation of CH₃Cl and CH₂Cl₂ were also determined. In a study of CH₃Cl oxidation, chemical activation effects were shown to be central to the chemistry of the CH₂ClO radical (produced in the reaction of CH₂ClO₂ with NO), with prompt decomposition (via either Cl-atom elimination or HCl elimination) accounting for about 40% of the chemistry.

The gas-phase reactions of both BrONO₂ and ClONO₂ with O₃ were studied using FT-IR spectroscopy, and upper limits for both rate coefficients were obtained, 1×10^{-20} cm³ molecule⁻¹ s⁻¹ in the case of BrONO₂ and 4×10^{-21} cm³ molecule⁻¹ s⁻¹ in the case of ClONO₂. These data show that both reactions are of negligible importance in the atmosphere.

Uptake coefficients for ClONO₂ on sub-micron liquid sulfuric acid aerosols were obtained as a function of aerosol acid content. The uptake coefficients ranged from about 7×10^{-2} at 36 weight % to 1×10^{-2} at 54 weight %, in general agreement with previously reported values and in accord with recent models of heterogeneous reactivity.

The formation of HCl from the reaction of OH with ClO has long been proposed, both to resolve model/measurement discrepancies in inorganic chlorine partitioning and to resolve ozone production/loss imbalances in the middle stratosphere. Preliminary experiments conducted at room temperature show small (2-8%) but significant and reproducible yields of HCl from this reaction, which are of the same order as required to resolve the discrepancies.

BrONO was identified for the first time in the gas phase, and was shown to be the major product formed in the reaction of Br with NO₂. A UV spectrum of BrONO has been obtained, which shows that this species will be lost very rapidly in the atmosphere via photolysis.

Photolysis of species such as HNO₃, HO₂NO₂, and H₂O₂, via absorption in OH overtone bands, has recently been proposed as a source of HO_x in the lower stratosphere at high solar zenith angles. To quantify the effects of these processes, absorption cross sections were determined for the OH overtones ($\nu = 3-5$) of a number of species (including HNO₃ and a series of alcohols). Overtone intensities were roughly independent of the absorber for a given vibrational level, and were found to decrease by about an order of magnitude with each successive vibrational level. The effect of HNO₃ photolysis via overtone excitation appears to be minimal.

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Laboratory Investigations of Stratospheric and Upper Tropospheric Chemistry

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Research Objectives

The primary objective of this project has been application of state-of-the-art experimental methods to investigate the kinetics, mechanisms, and thermochemistry of chemical reactions that play important roles in stratospheric and upper tropospheric chemistry. Secondary objectives include contributing to our understanding of atmospheric chemistry and chemical reactivity.

Summary of Progress and Results

One focal point of our research effort has involved development and implementation of flash photolysis schemes for studying radical-radical reactions of atmospheric interest. Our most recent efforts in this area have focused on the HO₂ + XO reactions, where X is a halogen atom. These studies involve simultaneous time-resolved detection of HO₂ (by tunable diode laser absorption spectroscopy) and XO (by UV-visible absorption spectroscopy). We obtained a 298 K rate coefficient of $2.0 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ for the HO₂ + BrO reaction, thus helping to decrease the undesirably large uncertainty in this important stratospheric reaction rate. We also carried out the first study of the temperature dependence of the HO₂ + IO rate coefficient, thus demonstrating that this reaction is considerably faster than previously thought, particularly in the (cold) upper troposphere and lower stratosphere. If IO mixing ratios in the lower stratosphere are as high as 0.1 pptv, then the HO₂ + IO reaction will play an important role in ozone destruction in this region. Furthermore, it appears that the HO₂ + IO reaction exerts an important

influence on partitioning of HO_x radicals, i.e., on the HO₂/OH concentration ratio, in the marine boundary layer and possibly in other regions of the troposphere as well.

A second focal point of our research effort has been photochemistry studies of interest for understanding lower stratospheric chemistry. We have recently completed a detailed study of bromine nitrate (BrONO₂) photochemistry and reaction kinetics; the role of this key species in stratospheric chemistry is critically dependent on the identity of the photodissociation products. At wavelengths longer than 300 nm, which are of primary atmospheric interest, we find that Br + NO₃ is the major photolysis channel, but BrO + NO₂ are also produced with a yield of about 0.2. We have measured temperature-dependent rate coefficients for the reactions of Cl, Br, and O atoms with BrONO₂. The O + BrONO₂ reaction is fast enough to compete with photolysis as a BrONO₂ destruction pathway at altitudes above 25 km; this rate coefficient, $k = 2.0 \times 10^{-11} \exp(205/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$, should be included in models in order to partition BrO_x correctly in the 25-35 km altitude regime.

A third focal point of our research effort has involved the application of chemical kinetics studies to evaluation of free radical thermochemistry. In collaboration with M. L. McKee, an ab-initio quantum chemist, we have carried out extensive studies of the stability and structures of radical-haloalkane adducts of atmospheric interest. Iodoalkanes, particularly those with electron-donating substituents, form particularly strongly-bound adducts, while adduct bond strengths vary as a function of the adding radical in the order F > Cl > Br, OH. These adducts have interesting structures (C-X-R bond angles around 90° where X is the halogen atom in the haloalkane and R is the adding radical) which suggest the formation of 2 center – 3 electron bonds. In addition to the studies described above, we have also completed studies of the kinetics of the forward and reverse reactions Br + C₂H₄ \leftrightarrow C₂H₄Br and Br + C₂H₆ \leftrightarrow C₂H₅ + HBr. The Br + C₂H₄ reaction is of interest in polar lower tropospheric chemistry, and a major controversy currently exists in the chemical kinetics literature concerning the magnitude and temperature dependence of the C₂H₅ + HBr reaction.

Publications

Over the last three years, six journal publications, two Ph.D. dissertations, and one Masters thesis describing work carried out on this project have appeared in print (references are given below). In addition, six other papers describing research discussed above are in various stages of preparation, and will ultimately be published.

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Laboratory Studies of Chemical and Photochemical Processes Relevant to Stratospheric Ozone

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Research Objectives

The purpose of this project is to reduce the uncertainty in key gas-phase kinetic processes which will improve our understanding of upper atmospheric ozone formation and destruction. The main emphasis of this work is to determine rate coefficients and product channels for reactions of HO₂ and RO₂ radicals in the temperature range 200 K to 240 K relevant to the lower stratosphere and upper troposphere. Other areas of study have included kinetic measurements of OH radicals with alternative halocarbons to determine their atmospheric lifetimes, and infrared spectroscopic studies of the HOCl molecule which can be used for remote sensing of stratospheric concentrations. The results of these studies will improve models of upper atmospheric ozone chemistry and predictions of perturbations due to human influences.

Summary of Progress and Results

HO₂ Radical Reactions: Kinetic measurements of the atmospherically important HO₂ + NO₂ and HO₂ + O₃ reactions at stratospheric temperatures (200-300 K) and pressures (50-200 Torr) have been performed using turbulent flow tube reactor with infrared tunable diode laser absorption to detect radical species. The HO₂ + O₃ rate coefficients are the first direct kinetic measurements of this reaction at temperatures below 235 K and show curvature in the Arrhenius plot indicating a faster reaction rate constant at the temperatures of the lower stratosphere than predicted from linear extrapolation of previous data. The HO₂ + NO₂ kinetic measurements are the first made at temperatures below 228 K and should result in a more accurate expression for the pressure and temperature dependence of the rate coefficient for this reaction. Operation of the flow tube reactor in the turbulent regime allows for HO₂ kinetic measurements at higher pressures (50-200 Torr) and lower temperatures (<235 K) than possible with conventional laminar flow tube kinetic measurements. Extension of this work to examine reaction rates for other peroxy-radical reactions important in the upper troposphere and lower stratosphere is in progress.

OH Reaction Rates with Alternative Halocarbons: The OH reaction rate coefficients for partially hydrogenated halocarbon substitutes determine their atmospheric lifetimes and ozone depletion potentials (ODPs). The global warming potential (GWP) for the compound depends on the atmospheric lifetime of the species as well as on its infrared spectrum. The temperature dependent rate constant for the reaction of the OH radical with 1-bromopropane has been measured using the discharge flow technique with laser induced fluorescence detection of the OH radicals. Rate constants were measured as a function of temperature between T = 271 K and T = 363 K. The temperature dependence is well described by a simple Arrhenius expression, $k(T) = A \exp[-E/(RT)]$ with $A = (5.75 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E/R = 504 \pm 50 \text{ K}$. The reaction rate at T = 277 K is $9.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which implies that the atmospheric lifetime is approximately 15 days. The quantitative infrared spectrum for 1-bromopropane has also been obtained using a Fourier transform spectrometer. Together with the atmospheric lifetime estimate, this spectrum implies global warming potentials of 1.0, 0.3, and 0.1 for integration time horizons of 20 years, 100 years, and 500 years, respectively. The ozone depletion potential (ODP) for bromopropane based on the kinetic results using a 2-D model and using the standard semi-empirical approach. The semi-empirical calculation of the ODP, using the 15-day lifetime and the model calculated vertical profile of 1-bromopropane, gives 0.0019. However, the 2-D model result is 0.027 using a fixed mixing ratio boundary condition for 1-bromopropane. It is likely that the semi-empirical method is inappropriate for species with lifetimes as short as 15 days.

Quantitative Infrared Spectroscopy of Stratospheric Molecules: Rotational line broadening coefficients in air are one of the quantitative parameters required to determine absolute concentrations of upper atmospheric trace gases from high resolution infrared absorption spectra. We have measured the air broadening coefficients for two infrared absorption lines of the v_2 band of HO³⁵Cl, the $8_{1,7} \leftarrow 7_{1,6}$ and $14_{1,14} \leftarrow 13_{1,13}$ lines at 1247.3169 and 1252.8437 cm⁻¹, respectively. We obtain values of 0.112 cm⁻¹ atm⁻¹ (half width half maximum) for the J'' = 7 line and 0.0955 cm⁻¹ atm⁻¹ for the J'' = 13 line. These measurements were made over a pressure range from 2 to 200 Torr using a high-resolution tunable diode laser system with an optical path length of 100 m. The results of these measurements are essential for the quantitative measurements of HOCl by infrared absorption in the upper atmosphere.

NASA Data Evaluation Panel: C. E. Kolb has served on NASA's Panel for Data Evaluation as the panel's lead member responsible for heterogeneous processes. The heterogeneous chemistry section of the biennial review, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, first introduced in 1990 and updated in 1994, has been revised and significantly expanded in the twelfth [DeMore *et al.*, 1997] edition. The Heterogeneous Chemistry Section now includes data tables covering Mass Accommodation Coefficients, Gas/Surface Reaction Probabilities, and Henry's Law Constants for Gas-Liquid Solubilities, as well as text and extensive notes presenting background and guidance for using the tables. The twelfth edition of the Heterogeneous Chemistry section presents and evaluates the work for over eighty new or revised archival publication beyond the eleventh edition.

In 1998 and the first half of 1999, Kolb, assisted by D. R. Worsnop and Q. Shi, reviewed all of the data for the six most important heterogeneous halogen activation and denitrification reactions as listed the WMO's Scientific Assessment of Ozone Depletion: 1998. All published data for the six reactions: hydrolysis of N₂O₅, ClONO₂, and BrONO₂, plus the reactions of ClONO₂, HOCl,

and HOBr with HCl, on water ice, nitric acid trihydrate (NAT), and sulfuric acid/water were collected and reevaluated. The data for N₂O₅ and ClONO₂ hydrolysis and the reactions of ClONO₂ and HOCl with HCl on sulfuric acid surfaces at various temperatures and acid wt. % were all fit to a previously published liquid phase uptake/bulk reaction model developed at Aerodyne for the hydrolysis reactions coupled with a consistent model for HCl uptake and solubility. This exercise yielded gratifying fits to essentially all of the published data for these reactions which were evaluated to be free of saturation effects. The model fit allowed quantitative recommendations of reactive uptake coefficients for all four reactions at arbitrary sulfuric acid aerosol temperatures and compositions as well as a much more quantitative analysis of the probable uncertainty in these recommended rate parameters. The updated recommendations for all six reactions will be posted on the NASA JPL Kinetics Evaluation web site by the end of 1999.

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B. SPECTROSCOPY



Quantitative Infrared Spectroscopy of Minor Constituents of the Earth's Atmosphere

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Research Objectives

Quantitative laboratory spectroscopic measurements are made on molecular constituents which are important in understanding the "health" of the Earth's atmosphere. Our measurements provide line intensity, shape, shift and frequency parameters at physical conditions appropriate for the real atmosphere. A parallel effort seeks to develop hyper-sensitive methods for detecting free-radical species important in atmospheric chemistry.

Summary of Progress and Results

Papers were published on nitric oxide line parameters; these papers include the first measurements of any kind on the molecular oxygen broadening in infrared bands of NO. For the purpose of magnetic rotation (MR) detection of NO₂, infrared Zeeman tuning parameters were determined for this molecule. Using a Herriott multiple reflection cell built into a solenoid magnet, we applied MR to the detection of NO and achieved sensitivities of ppt/sec. A comprehensive study on the 6.7 μm spectral region of methyl chloride was completed with thousands of lines assigned for the chlorine 35 and 37 isotopic species with line positions and ground and excited rovibrational state parameters determined. New intensity results were obtained for the first and second vibrational overtones of carbon monoxide. These results, along with those planned for the fundamental, will lead to an improved electric dipole moment function for carbon monoxide and revision of the HITRAN data base of CO line intensities. Significant errors listed in the HITRAN and GEISA databases were discovered for water line intensities listed for the visible-near-infrared spectral region. Our recent laboratory measurements of line intensities done in the 1720 cm⁻¹ band of HNO₃ are inconsistent with published values (by 30%) and will be repeated to check our consistency. Some progress has been made in obtaining OH emission spectra with a good relative intensity calibration over the 2800-8700 cm⁻¹ range.

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Tunable Far Infrared Studies in Support of Stratospheric Measurements

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Research Objectives

This program provides fully line-resolved measurements of submillimeter and far infrared spectroscopic line parameters (pressure broadening coefficients and their temperature dependences, and line positions) for the analysis of field measurements of atmospheric constituents, far infrared database improvements, and studies for improved satellite measurements of the Earth's atmosphere. This program is designed to enable the full utilization of spectra obtained in far infrared/submillimeter field measurements, such as FIRS-2, FILOS, IBEX, SLS, EOS-MLS, and proposed NASA and European Space Agency measurements of ClO and OH (e.g., PIRAMHYD and SFINX) for the retrieval of accurate atmospheric altitude profiles of key trace gases involved in ozone layer photochemistry.

Summary of Progress and Results

For the analysis of the spectra obtained in the atmosphere from far infrared measurements it is necessary to have accurate values of the molecular parameters (line positions, strengths, and pressure broadening coefficients) for the measured molecules and for possible interfering species. Knowledge of line positions is in increasingly good shape, with some notable exceptions. The increase in position information includes research that has been performed in the present program of research on OH, HO₂, H₂O, H₂O₂, O₃, HCl, HF, HBr, HI, CO, NO, FO, and ClO. Knowledge of strengths is in generally good shape, since most of the lines are from electric dipole transitions whose intensities are well determined from Stark effect measurements; exceptions include some molecules with large vibration-rotation interactions (NO₂) and internal motions (H₂O₂ above the lowest torsional state). The line parameters that are still the least well determined are pressure broadening coefficients, and their temperature coefficients. These are strongly dependent on the quantum states involved in the transitions, in a way that is much more

complex than the simple projection by directional cosine matrix elements involved in determination of rotational line strengths from static dipole moments.

Developmental work in ultra-high-resolution spectroscopy using the TuFIR method accomplished during this period includes:

- Development of instrument control and data acquisition software, allowing for precise control of the TuFIR instrument parameters and long integration times for weak spectral lines;
- Development of Hamiltonian fitting capability that includes asymmetric top molecules with electron spin-rotation interactions, up to high degree in centrifugal distortion, and nuclear hyperfine (spin-spin dipolar, Fermi contact, and nuclear quadrupole) interactions;
- Development of lasers and of MIM diode mixing technology permitting TuFIR measurements in the 6-9 THz range. We now generate 9 THz radiation by using a 13 micron (23 THz) $^{15}\text{NH}_3$ laser and a CO₂ laser at 9 microns (32 THz) irradiating the MIM diode. We use a higher frequency photoconductor detector to increase the measurement sensitivity at 9 THz;
- Evaluation and testing of detector sensor elements at these high frequency regions; and
- Design and fabrication of a tunable cold grating filter system. The laboratory detector performance will improve by an order of magnitude when this filter system is implemented. The design is finished, and most components have been fabricated. Assembly and final testing is in progress.

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Millimeter and Submillimeter Spectroscopy in Support of Upper Atmospheric Research

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Research Objectives

A program of millimeter and submillimeter spectroscopy research is conducted in support of upper atmospheric research. This includes laboratory studies, critical analysis of data from all available sources, generation of line list catalogs, and distribution of results to the field measurement community. The program involves the acquisition and analysis of molecular spectral parameters, which are required for the interpretation of data from stratospheric measurements. The laboratory spectral measurements specifically support the JPL millimeter radiometer instruments. In order to take full advantage of spectroscopic techniques for quantitative atmospheric measurements, emphasis is placed on performing accurate line frequency, line width, and transition moment measurements. A large portion of the spectral data is also of value to other groups, which use spectroscopic techniques for atmospheric measurements. These data are cataloged in a continuously upgraded millimeter database and made available to interested users. This program also provides rotational spectra of ground and excited states of molecules whose infrared spectra are observed in the upper atmosphere. The fitting algorithms developed for this program are also used to analyze vibrational spectra. In addition, this program provides valuable molecular structural and reaction product distribution information, which has direct bearing on proposed mechanisms for polar ozone destruction. Elucidation of the molecular properties of the halogen oxides and oxo-acids is a continuing objective of these investigations.

Summary of Progress and Results

The rotational spectra of the four main isotopomers of ClClO₂ have been observed and analyzed. The molecular structure, quadrupole coupling constants, dipole moment and harmonic force field have been determined. Two papers on this second stable conformer of ClO dimer have been published. A review of spectra gathered during our earlier studies of the peroxide form of ClO dimer, ClOOCl, shows no indication of ClClO₂ features. The rotational spectra of the two lowest vibrational fundamentals have been analyzed and those results are being prepared for publication.

Analyses of spectra gathered during the ClClO₂ study and our previous ClOClO₂ work has resulted in a publication of improved parameters for OCIO. Spectra of FCIO₂ gathered during the ClClO₂ study have been analyzed and are being prepared for publication.

Work has been completed on the rotational spectra of the three main isotopic species of BrOBr and the excited bending state of the mixed isotopomer. A paper describing the spectra, molecular structure, harmonic force field, and quadrupole coupling tensor has been published.

The rotational spectra of OBrO in its ground and two lowest excited bending states have been observed and analyzed. A thorough treatment that includes a determination of the molecular structure, dipole moment, fine and hyperfine structure constants and their interpretation has been published.

The rotational spectrum of the $X_1^2\Pi_{3/2}$ state of IO was observed in highly excited vibrational states ($v \leq 12$) in a chemiluminescent reaction of I₂ and the products of an oxygen discharge. In a DC discharge the spectra of the $X_1^2\Pi_{3/2}$ state was extended to $v = 13$, and the $X_2^2\Pi_{1/2}$ state was observed for the first time and followed to $v = 9$. I¹⁸O was observed to $v = 5$. The interatomic potentials for both the $X_1^2\Pi_{3/2}$ and $X_2^2\Pi_{1/2}$ states have been well determined and an extensive set of molecular parameters has been derived.

OIO has been identified as a byproduct of the IO chemistry. Its rotational spectra in the ground and lowest excited bending state have been observed and analyzed. This is the first high-resolution spectral observation of the molecule. The molecular structure, harmonic force field, and hyperfine parameters have been determined.

Rotational spectra of highly excited BrO up to its $X_1^2\Pi_{3/2}$, $v = 8$ and $X_2^2\Pi_{1/2}$, $v = 7$ states have been observed in a DC discharge. Br¹⁸O was also observed. The BrO interatomic potential and molecular parameters have been improved.

Cl¹⁸O rotational spectra have been observed for the first time as have spectra of ClO in the $v = 2$ state. As a result of the isotopic substitution the electron spin-rotation constant has been determined for the first time.

The millimeter spectrum and Stark effect of FCIO have been measured. The molecular structure, dipole moment and hyperfine constants have been determined.

A number of calculations in the JPL *Microwave Millimeter and Submillimeter Spectral Line Catalog* have been updated or improved. Among them are those for the following molecules: BrO, OBrO, ClClO₂, OCIO, ClONO₂, SO₂, SO₂ $v_2 = 1$, ¹⁸OSO, ³⁴SO₂, and ClNO₂.

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Millimeter and Submillimeter Spectroscopy of Molecules of Atmospheric Importance

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Research Objectives

It has been demonstrated that remote sensing techniques based upon millimeter, submillimeter and infrared technology can make important contributions to atmospheric science. The planning, execution, and interpretation of those experiments require a firm knowledge of the spectroscopic properties of atmospheric molecules. Our work is designed to support these atmospheric observations via contributions to the spectroscopic data base for the microwave through infrared spectral region. The work includes both the direct measurement of spectra of important atmospheric species and the calculation of synthetic spectra from these measurements. Results include line positions, linewidths, and intensities in both the ground and excited vibrational states.

Summary of Progress and Results

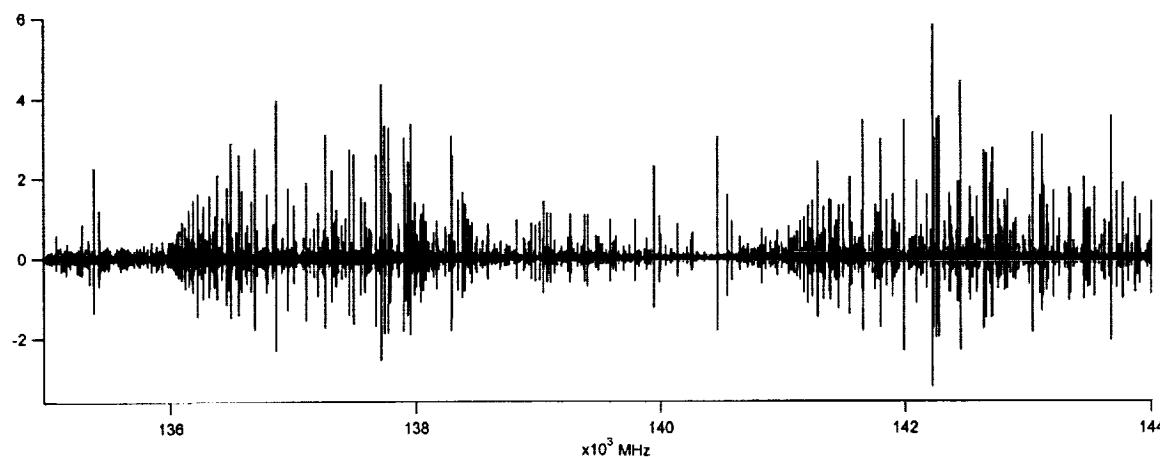
Hydrogen peroxide is one of the species in which we have had a long-term interest. Our earlier work on the millimeter and submillimeter (mm/submm) spectrum of this species established the procedures which are currently used for the analysis of the entire rotational-vibrational spectrum of this species. In our latest work (described in more detail in the publication list below), we have been able to include both extensive new mm/submm measurements in both the ground and excited torsional and vibrational states with infrared (IR) measurements in a weighted, joint analysis. This analysis accurately characterizes the spectrum in both spectral regions to their respective experimental uncertainties. This is illustrated in the table.

We have also had a long-term interest in the spectrum of nitric acid. Again, we initially analyzed its ground state rotational spectrum in the mm/submm, with later work on the excited vibrational states beginning with the lowest energy state (v_9) and working up in vibrational energy. Because of the importance of the $2v_9/v_5$ dyad in atmospheric remote sensing and because of its complex and crowded spectrum in the infrared, we have focused recently on the mm/submm rotational-torsional spectrum of this dyad. This dyad also serves as a stringent test of the hypothesis that the spectra of similar molecules (or heavier molecules with marginally resolved or unresolved spectra in the infrared at the Doppler limit) can be successfully synthesized to high accuracy from analyses of rotational spectra of both their ground and excited vibrational states.

Statistical Summary of Data Sets Included in the HOOH Analysis

Type of Data	States	Number of Data	Rms Deviation
Microwave, mm/submm-wave rotational-torsional transitions	$v = 0; n = 0,1$ $\tau = 1,2,3,4$	573	0.088 MHz
mm/submm-wave rotational-torsional transitions	$v_3 = 1, n = 0$ $\tau = 1,2,3,4$	148	0.103 MHz
submm-wave rotational-torsional transitions	$v = 0; n = 0,1$ $\tau = 1,2,3,4$	64	0.073 MHz
submm-wave rotational-torsional transitions	$v = 0; n = 0$ $\tau = 1,2,3,4$	61	0.060 MHz
IR energy levels	$v = 0, n = 0,1,2,3$ $v_3 = 1; n = 0,1$ $\tau = 1,2$	1473	0.00071 cm^{-1}
IR energy levels	$v = 0; n = 0,1,2,3$ $v_3 = 1; n = 0,1$ $\tau = 3,4$	1162	0.00047 cm^{-1}
IR combination differences	$v = 0; \tau = 1,2$	376	0.00068 cm^{-1}

We have now completed an analysis of about 2000 mm/submm transitions of HNO_3 , used the results to synthesize the rotational structure of the infrared band and compared the results of the synthesis to the very high quality infrared energy levels which are available. Briefly stated, the quality of the synthesis is such that the distribution of differences between its *predictions* of the infrared energy levels is not distinguishable from the distribution of residuals of the *fit* to the infrared data which produced them. Additionally, for the large majority of the levels, those derived from the microwave analysis should be much better because the mm/submm fit is about two orders of magnitude better than the infrared fit. We expect that the paper which describes this work will be completed before the end of the year.



Spectrum of ClONO_2 between 135 and 144 GHz.

Based on these results, we have begun a series of studies on ClONO₂. The infrared spectrum of this somewhat heavier species is either marginally resolved or unresolved at the Doppler limit. We have now succeeded in assigning and analyzing the rotational spectra of this species in six different vibrational states. This work has been greatly aided by the Fast Scan Submillimeter Spectroscopy Technique (FASSST), which we have developed. The figure above shows a small portion of the spectrum (recorded in about a second) and illustrates the spectral density of ClONO₂ even in the mm/submm. However, the resolution of the FASSST system is much greater than can be plotted here. To show all of the individual lines, even the small segment shown in the figure would have to be blown up by about a factor of 100. Some of this work is described in the publication listed below, and we expect that more of these results will be published later this year.

Our work also includes the study of broadening parameters. Perhaps the most broadly significant is the intercomparison between some of our measurements and measurements of the same transitions made at JPL, but with a rather different methodology. This work showed that the agreement between these measurements, which can truly be characterized as 'typical', is very good, 3%.

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Infrared Spectroscopic Studies of Atmospheric Molecules

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Research Objectives

Laboratory spectra of atmospheric molecules are measured to provide accurate line frequencies and intensities for modeling atmospheric spectra recorded by ground and space-based instruments. Both laser and Fourier-transform techniques are used to provide a wide range of spectral coverage, resolution, and sensitivity. Laboratory spectra investigated include the allowed and collision-induced 1.27 μm near-infrared bands of molecular oxygen (O_2) and various midinfrared bands of hydrofluorocarbons (HFCs), sulfur dioxide (SO_2), chlorine nitrate (ClNO_3), and carbonyl fluoride (COF_2).

Summary of Progress and Results

A major part of our effort has been devoted to the laboratory investigation of the sharp and collision-induced-continuum features of the 1.27 μm $a^1\Delta_g - X^3\Sigma_g^-$, $v = 0 - 0$ midinfrared absorption band of O_2 . The discrete band had been identified in the atmosphere a number of years ago in absorption against the solar background [Herzberg and Herzberg, 1947], while only recently has the continuum feature been seen [Mlawer *et al.*, 1998]. Both the discrete and continuum bands play an important role in the near infrared absorption of the atmosphere, and additionally, the discrete band atmospheric emission is used for ozone concentration determinations in the mesosphere and thermosphere by the Solar Mesosphere Explorer (SME) satellite and the soon to be launched Thermosphere Ionosphere Mesophere Energetics and Dynamics (TIMED) satellite.

The $a^1\Delta_g - X^3\Sigma_g^-$ discrete band is responsible for ~10% of the O_2 contributed heating of the tropopause [Mlynczak and Marshall, 1996]. Moreover, it has been recently suggested [Murcray *et al.*, 1997] that O_2 continuum absorptions, not generally included in atmospheric modeling codes or spectroscopic databases such as HITRAN, may be responsible, in part, for the discrepancy between model calculated and observed atmospheric short-wavelength absorption. However, more recent studies of these bands indicate that they contribute approximately 0.42 W m^{-2} to the globally averaged absorption of the sun by the Earth's atmosphere [Mlawer *et al.*, 1998], significantly less than the 10 W m^{-2} to 30 W m^{-2} discrepancy between general circulation models and observations [Wild and Liepert, 1998; Arking, 1996]. Although they alone are not responsible for the model discrepancy, the near-infrared oxygen continuum bands still account

for approximately 1 % of the 55 W m^{-2} of globally averaged clear sky atmospheric absorption. Their effect is similar in magnitude to the total radiative forcing of anthropogenic CO_2 , CH_4 , N_2O , and the halocarbons (2.5 W m^{-2}) [Intergovernmental Panel on Climate Change (IPCC), 1997] and is of the same size as the 1 W m^{-2} accuracy for radiation flux measurements and models desired by some [United States Department of Energy, 1996]. When combined with O_2 continuum absorptions in the visible and near ultraviolet, a global average clear-sky absorption of $.53 \text{ W m}^{-2}$ to 1.22 W m^{-2} is obtained [Pfeilsticker *et al.*, 1997; Solomon *et al.*, 1998; Mlawer *et al.*, 1998], indicating the importance of the near-infrared bands to the total short-wavelength solar continuum absorption by O_2 .

To provide spectroscopic line intensities and frequency information for the discrete and continuum bands were have measured the $1.27 \mu\text{m}$ absorption band using a Fourier-transform spectrometer and an 84 m optical path through O_2 and O_2/N_2 samples at pressures up to 10 atm to increase the contribution of the continuum feature which grows with the square of the pressure. A precise band strength determined for the discrete feature differs by $\sim 15\%$ from the HITRAN 96 value based on the Einstein A coefficient of Gamach, Goldman, and Rothman [1998] determined from an analysis of the solar spectrum of Wallace and Livingston [1990]. We note that a 15% error in the band strength corresponds to a 15% error in retrieved O_3 concentrations based on monitoring the $\text{O}_2 \alpha ^1\Delta_g$ atmospheric emission. Our measurements on the continuum band also reveal large discrepancies for the binary $\text{O}_2\text{-N}_2$ collision-induced coefficient from previous measurements of more than 25 years ago [Choe *et al.*, 1963]. In addition our air results for the continuum band strength differ significantly from a recent value determined by Mlawer *et al.* [1998] from the atmospheric spectrum. At present this discrepancy is not understood.

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Calibration Facilities for NASA at SURF II (now SURF III)

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Research Objectives

It is critically important to have a common radiometric base for the wide range of scientific missions being carried out by rocket, by satellite, and on the space shuttle. It has been demonstrated that this can be achieved by using the NASA Spectrometer Calibration Facility at SURF III, the Synchrotron Ultraviolet Radiation Facility, at the National Institute of Standards and Technology. This beamline, with its large spectrometer calibration chamber, utilizes the calculable nature of synchrotron radiation to calibrate a wide range of spectrometer and photometer systems, thereby serving as a common radiometric base. The accuracy of this calibration source has been thoroughly documented and is adequate to this task.

Summary of Progress and Results

Twelve NASA related calibrations were performed at the NASA/SURF Spectrometer Calibration Facility at NIST during the period from 1997 through 1999. Users of the facility included: T. Woods (three times), CU/LASP (EUV Grating Spectrograph); D. Judge (eight times), USC/SSC (Solar EUV Monitor and Solar EUV Hitchhiker); and D. Hassler (one time), SwRI (Calibration and Test Equipment 3).

Several years ago we began planning to upgrade the accelerator to further improve the radiometric performance, both in accuracy and spectral range. The upgrade of the new magnet system has been completed and SURF III is now in operation. Testing of the magnet system has shown the capability of operating from 73 MeV to 417 MeV with better than $\pm 0.03\%$ azimuthal uniformity of magnetic field strength without the use of trim coils. This should result in absolute flux uncertainties of better than 1% from 2 nm to beyond 400 nm. The storage ring is now being operated at an electron energy of 331 MeV rather than the 284 MeV energy of SURF II. This results in a significant increase in the flux at soft x-ray wavelengths. Measurement of vertical beam motion in going from an electron energy of 331 MeV to 183 MeV shows a factor of eight improvement over that of SURF II. The lower energy is used for order sorting in grating instruments. In order to decrease the uncertainty in beam current information, improvements

have also been made to the beam current monitoring system and the method used for electron counting.

A new initial vacuum gate valve was installed on the calibration beamline and oriented to minimize radiation damage to the seal from the photon beam. In order to compensate for a small angular change in the storage ring orientation, which was necessitated by the addition of new magnetic field probe ports and new beamline ports to the storage ring vacuum chamber, the entire front end of the calibration beamline was redesigned. The new design included a dual aperture plate machined directly onto a vacuum gasket to insure accurate positioning. The dual aperture provides for an auxiliary port on the beamline which can be used to examine properties of the radiation source near the same tangent point as that of the main port. Also redesigned were the baffles used to prevent scattered light from entering user instrumentation and apertures used to limit the light illuminating the defining orbital plane locator aperture located at about 10.4 m from the tangent point. The distance from the tangent point to this aperture was measured for the first time to an accuracy of ± 1 mm ($\sim 0.01\%$). A laser rangefinder was obtained so that other distances along the beamline can now be measured with an accuracy of ± 1.5 mm.

A number of improvements were made at the milling table station. New glass scale linear encoders and a readout were acquired for the vertical and horizontal motions which have reference marks that are used to provide absolute position information in the event of a power outage. The milling table station now has fully dedicated motion control and position readout. The new components required a revision to the software for the motion control system. A new digital ion gauge controller was procured with an IEEE-488 interface for communications. The ranges of motion on both the pitch and yaw axes were extended to $\pm 7^\circ$ and the linear encoders calibrated to accommodate the larger range. A high-resolution (1 μ rad) tiltmeter was installed on the pitch frame to provide a backup absolute readout for the pitch angle.

Reorientation of the cryopump near the milling table station has resulted in a significant improvement in pumpdown times. In the past all users, after initially hooking up to the beamline, were required to wait a minimum of several days before achieving passing residual gas levels. Now, more than one user has been able to reach initial passing residual gas levels after pumping only overnight. Also a number of users who rotated their instruments to the orthogonal roll orientation necessary to simulate unpolarized light, have reached passing residual gas levels after overnight pumpdowns.

There were several other improvements to vacuum systems. There is now additional cryopumping capability for the large vacuum chamber. A new mobile ultrahigh vacuum pumping/test station was fabricated which includes a cryopump, a large ion pump, a residual gas analyzer, isolation and roughing valves, and a large chamber with multiple sized ports. A new flexible bellows coupling was obtained for interfacing to user instrumentation to replace a damaged one.

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A Facility for High-Resolution Spectroscopy: Laboratory and Ground-Based Observations in Support of Upper Atmospheric Research

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Research Objectives

This research contract consists of operating a facility for the purpose of obtaining high-resolution spectroscopic observations in support of upper atmospheric research. The facility responds to the specific needs and interests of the visiting investigators. The research objectives are twofold: 1) laboratory studies devoted to determining line-shape parameters for radiative transfer calculations that interpret remote sensing data, and 2) the collection of ground-based atmospheric data with the McMath-Pierce solar telescope. The success of these studies rely on the unique advantages of the McMath Fourier transform spectrometer (FTS): high spectral resolution (0.0025 cm^{-1} @ $10 \mu\text{m}$), wide spectral coverage ($600\text{-}30000 \text{ cm}^{-1}$), high signal-to-noise ratios (1000:1), and short integration times ($\leq 1 \text{ hour}$). In addition, line centers from recorded FTS spectra can be measured to an absolute accuracy of 0.00005 cm^{-1} while line intensities to a relative accuracy of 3%.

Summary of Progress and Results

In support of atmospheric remote sensing from space, aircraft, balloons, and the ground, high-resolution laboratory absorption spectra in the range from 600 to 14000 cm⁻¹ were obtained with the McMath FTS for the following molecules: CH₄, CH₃, CH₃Cl, CH₃OH, CO, CO₂, D₂O, H₂O, HDO, H₂S, O₂, O₃, OH, NH₃, HNO₃, NO, NO₂, N₂O, PH₃, and SO₂. Measurement and analysis of these spectra were performed by Linda Brown and Robert Toth at JPL; Chris Benner, Mary Ann Smith, Curtis Rinsland, and Malathy Devi at Langley; Charles Chackerian, Jr., and Larry Giver at Ames; and collaborators from institutions in Canada, France, and Russia.

At JPL, studies by Toth have focused on analyzing FTS spectra of H₂O and HDO from 590 to 2200 cm⁻¹, including the interacting hot bands of H₂¹⁶O present in this region and those centered around 3700 cm⁻¹, and the bands of N₂O from 1800-7800 cm⁻¹ to collect data on line positions and strengths, air-broadened linewidths, and pressure-induced line shifts for TES and AIRS. Line positions and intensities of the oxygen A-band at 13122 cm⁻¹ were measured by Brown in support of applications such as SAGE III that determine atmospheric pressure and temperature using this band. Analysis of the infra-red methane spectrum by Brown and collaborators from Langley and France have lead to the development of a model that can now accurately predict frequencies and intensities of ¹²CH₄, ¹³CH₄, and CH₃D lines in bands present in the region from 900 to 3400 cm⁻¹. A study is currently underway to extend the assignment of CH₄ lines for bands in the octal (3500-4800 cm⁻¹) and the tetradecad (4800-6500 cm⁻¹) regions of the spectrum. Research done on these abundant atmospheric species is in preparation for EOS (SAGE III, MOPITT, AIRS, and TES) and other future atmospheric remote sensing programs such as ACE.

The laboratory spectroscopy group at Langley, in addition to their collaboration on the analysis of the infrared methane spectrum, have also been involved in analyzing FTS spectra of ozone in the 10 μm region, specifically to determine absolute infrared-line intensities and to measure the temperature-dependent broadening and shifting of lines over the temperature range of 150-300 K.

In collaboration with Brown, Cohen, and Toth at JPL, Chackerian at Ames is in the process of analyzing HNO₃ infrared spectra recorded in 1996 with the McMath FTS to resolve existing discrepancies in measured line intensities involving the bands in the intervals near 900, 1300, and 1720 cm⁻¹ that are used by remote sensing. Completed studies by Chackerian *et al.* include the pressure broadening of NO lines in the fundamental band at 5 μm by O₂, analysis of the CH₃Cl band at 1500 cm⁻¹, measurement of Zeeman tuning rates for Q-branch lines in the v₃ band of NO₂ from spectra recorded with the McMath FTS and frequency-modulated diode lasers at Ames, and the measurement of rotational line intensities of the 3-0 band of CO that will be used in deriving an accurate electric-dipole moment function for the X⁺¹Σ⁺ ground state.

The second part of this research contract entails the collection of atmospheric data using the McMath-Pierce FTS in conjunction with the McMath-Pierce solar telescope as a means of monitoring the seasonal variation in the concentrations of targeted atmospheric species. In 1993 Kitt Peak was designated as an official complementary site for the Network for the Detection of Stratospheric Change (NDSC) in Lauder, New Zealand. Rinsland at Langley has been actively monitoring the surface concentrations of routinely targeted atmospheric gases such as O₃, CH₄, and CO for well over a decade from high-resolution solar infrared spectra recorded with the McMath-Pierce FTS at monthly intervals. In addition, this continuing study also includes 1)

measurement of the long-term trends in the concentrations of HF and HCl; 2) seasonal cycles, vertical distributions, and correlations between N₂O and CH₄; 3) comparisons of Kitt Peak and correlative measurements of CO total columns obtained during shuttle missions; and 4) comparative studies of simultaneous observations of CO, C₂H₂, C₂H₆ total columns from sites in the Northern and Southern Hemispheres.

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Middle Atmosphere Radiative Transfer: The Heat Budget, Coupling, and Photochemistry of the Stratosphere and Mesosphere

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Research Objectives

The primary goal of this effort is to conduct basic research on radiative transfer in the middle atmosphere and to evaluate the energy balance in the stratosphere using data from the Upper Atmosphere Research Satellite. A secondary goal is to develop the basic requirements for determining the energy budget of the mesosphere from future space-based measurements. The computation of radiation transfer and the evaluation of the energy balance in the upper atmosphere is complicated significantly by the occurrence of non-local thermodynamic equilibrium (non-LTE) in the processes of solar heating and infrared cooling. We have proceeded to evaluate the heat budget of the stratosphere, to define the needs for laboratory measurement of energy transfer parameters used in non-LTE modeling, to develop new techniques to compute rates of solar heating from observations of the airglow, and to evaluate existing datasets of limb radiance measurements of non-LTE emission. This work has paved the way for evaluating the energy balance of the stratosphere and mesosphere together in NASA's upcoming TIMED spacecraft mission.

Summary of Progress and Results

Stratospheric Energy Balance: The primary contribution to this topic is the analysis of 13 months of data from the Upper Atmosphere Research Satellite (UARS) and reanalysis of 7 months of data from the Limb Infrared Monitor of the Stratosphere. The results, presented in 2 papers [Mertens *et al.*, 1999; Mlynczak *et al.*, 1999], showed that the stratosphere is in global

mean radiative equilibrium on monthly timescales to within the accuracy of the UARS data and the radiative transfer calculations. Rates of solar heating due to absorption of radiation by ozone, carbon dioxide, and oxygen were included. Rates of cooling (10 to 3000 cm⁻¹) were computed for ozone, water vapor, and carbon dioxide. Infrared properties of the Pinatubo aerosol were also rigorously included using UARS-observed aerosol extinction values. The global mean rates of heating and cooling balanced generally to better than 0.1 K/day. This balance allowed confident calculation of the Lagrangian meridional circulation from the Eulerian heat budget without having to make large mass adjustments as has been required in previous studies of the stratospheric energy budget.

Some interesting details of the stratospheric heat balance emerged beyond the observation of global mean radiative equilibrium. In particular, it was demonstrated that overlap between the spectral lines of carbon dioxide and ozone is important and that neglect of this overlap in the radiative transfer calculations causes significant deviation from global mean radiative equilibrium. In addition, the presence of Pinatubo aerosols (which causes increased infrared heating) also serves to increase the radiative relaxation time in the lower stratosphere.

The results of these studies (heating rates, cooling rates, Lagrangian diabatic circulations are available at the Middle Atmosphere Energy Budget Web site at <http://heat-budget.gats-inc.com>.

Mesospheric Energy Balance: A frontier in atmospheric science research is the energy balance of the mesosphere, typically 50-100 km in altitude. We have been pursuing research in a number of areas in order to evaluate the mesospheric energy balance using new observations to become available with NASA's TIMED mission late in the year 2000. A new technique [Mlynczak, 1999] has been developed to measure the rate of energy deposition and heating in the mesosphere due to the absorption of ultraviolet solar radiation by ozone. The technique uses measurements of the molecular oxygen airglow emission at 1.27 μm and is independent of knowledge of the ozone density, the solar irradiance, and the ozone absorption cross sections. A more general assessment of the mesospheric energy budget and the approach to its observation and determination is given by [Mlynczak, 1997].

Significant progress has also been made in defining the accuracy to which numerous energy transfer rates must be known to allow accurate retrieval of temperature and minor species abundance from measurements of non-LTE infrared radiation [Mlynczak *et al.*, 1998, 1999; Mlynczak and Zhou, 1998]. Knowledge of rates of vibration-to-translation energy transfer are essential to accurate calculation of molecular vibrational temperatures under non-LTE conditions. Accurate retrieval of atmospheric structure from remote measurements of infrared emission is impossible unless the non-LTE energy transfer parameters are well-known. In these publications we have defined the requirements for various parameters for the express purpose of providing guidance to the laboratory kinetics community. In turn, as many as 9 proposals have been submitted to NASA and NSF in the 1997-1999 period to make the required measurements.

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Analysis of Atmospheric Spectra for Trace Gases

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Research Objectives

The main objective of this research is the analysis of IR solar spectra to obtain column and profile measurements of important atmospheric gases. Emphasis is the determination of long-term trends and seasonal cycles of molecules involved in O₃ chemistry. Secondary objectives include refinements to algorithms for retrievals from IR solar spectra, laboratory studies to improve spectroscopic parameters for atmospheric inversions, and updates to spectroscopic databases.

Summary of Progress and Results

High-resolution Network for the Detection of Stratospheric Change (NDSC) solar spectra recorded at Mauna Loa (Hawaii), Jungfraujoch (Switzerland), and Lauder (New Zealand) have been analyzed to determine seasonal cycles and trends of a number of important atmospheric gases. The work has been supplemented with analyses of atmospheric measurements obtained from the National Solar Observatory on Kitt Peak, Arizona, laboratory studies to improve spectroscopic parameters for atmospheric studies, and updates to the HITRAN compilation. A program (SFIT) developed for NDSC is widely used. An improved program (SFIT2) based on the Rodgers optimum estimation method yields improved retrievals and has been the basis of recent atmospheric studies.

Partial columns of N₂O, CH₄, O₃, and HNO₃ have been retrieved from Kitt Peak spectra for 2 layers, 14-20 and 20-50 km. Measurements of N₂O versus CH₄ for the 14-20 km layer show a compact positive correlation. No evidence was found for a variation in the relation with season. The 20-50 km of N₂O versus CH₄ 20-50 km columns also show a compact relation despite the shorter lifetimes of both molecules. Compact O₃ vs. HNO₃ relations are measured for the 14-20 km layer provided observations recorded shortly after the Mt. Pinatubo volcanic eruption are excluded. The N₂O-CH₄ and O₃-HNO₃ correlations closely match corresponding relations calculated from Atmospheric Trace Molecule Spectroscopy (ATMOS) profile measurements

recorded near the same latitude in November 1994, taking into account the more limited vertical resolution of the Kitt Peak measurements.

Free tropospheric CO, C₂H₆, and HCN columns have been retrieved from time series of Mauna Loa solar spectra. The 3.4-16 km columns of the 3 molecules were enhanced beginning in about September 1997 with the highest levels observed during November 1997. Back-trajectory calculations performed for November 1997 show the low northern latitudes of Asia as the most likely source of the emissions. As biomass burning is an important source for all 3 molecules and widespread burning occurred throughout southeast Asia at the time, we attribute the measured trace gas enhancements to emissions from those fires.

A paper describing the HITRAN 1996 database was written for a special issue of the *Journal of Quantitative Spectroscopy and Radiative Transfer*. Articles were also written documenting the HITRAN updates for O₃, NO, HNO₃, ClONO₂, HBr, HI, NO₂ and SO₂. Improved parameters for the C₂H₆ v₇ band ¹Q₃ subbranch have been used in several recent atmospheric studies.

About 30 peer-reviewed journal papers reporting stratospheric, tropospheric, and spectroscopic studies resulted from work on this NASA task (1997-1999). A partial list is given below.

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Laboratory Far-IR Quantitative Spectroscopy of Molecules of Atmospheric Relevance

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Research Objectives

Abstract for Proposal Submitted in 1996: Measurements of spectral parameters are proposed for molecules of atmospheric relevance, with particular emphasis in the 350-500 cm⁻¹ spectral region. A three-year research effort is proposed where emphasis will be primarily given to the pure rotational spectrum of H₂O and the v₉ region of HNO₃. Accurate determination of line frequencies, strengths, shapes and broadening is necessary for proper reduction of atmospheric data. A number of measurements has been selected which are of highest priority for atmospheric retrievals. This set involves spectral regions and conditions for which data is lacking or unreliable, and where our instrumentation presents unique advantages. A unique set of tools will be applied. Some of these tools are: tunable diode lasers working in the 3.5 to 30 μm range, blocked impurity band (BIB) detectors working in the 5 to 42 μm range, long path (8 to 800 m) multipass temperature controlled (coolable) cell, and Cesium Iodide beamsplitters to be used at the McMath Solar Observatory FTS instrument to extend its range to 55 μm. Other species will be included in our program as the need for spectral information is stated by atmospheric researchers, particularly for those problems where our instrumentation presents a clear advantage over more traditional instrumentation. Researchers within the UARP Program, who are currently performing field measurements, suggested the execution of the measurements proposed here, given the fundamental importance of these data for their work.

Summary of Progress and Results

HNO₃: v₉ Fundamental: Line intensities for the v₉ fundamental in HNO₃ were obtained and reported [Sirota *et. al.*, 1997]. Absolute line intensities for the v₉ fundamental (458.228 cm⁻¹) in HNO₃ were determined for the first time, using tunable diode laser spectroscopy. This technique permitted short integration times, proven important to avoid dissociation in this highly reactive species. Thirty-eight transitions belonging to P and R branches were measured. The absolute

value of the transition dipole moment was determined to be 0.2561(21) debye, yielding a value for the integrated band intensity at 296°K of 209 cm⁻² atm⁻¹. Several tests demonstrated the absence of decomposition during the measurements, an unavoidable problem in previous FTS measurements in this region. A value for the square dipole moment was obtained. The line intensities are 36% smaller than those listed in HITRAN '92. Goldman and Rinsland assigned an uncertainty of up to 15% to the HITRAN values. The original source of the HITRAN values was a broadband measurement for the whole 22 μm region. Contamination from bands other than v₉ which also fall in the same region was not included in that analysis and this may have caused an overestimation of v₉ intensities.

High-Resolution Infrared Spectrum of the 3v₉–v₉ Hot Band of HNO₃: Study of Coriolis Coupled 3v₉ and the Nearby Dark State: The high-resolution infrared spectrum of HNO₃ in the region of 805 – 853 cm⁻¹ has been measured and assigned for the 3v₉–v₉ hot band. The significant splittings in the upper state 3v₉ arising from the torsional motion of H around ON were observed and identified. It was found that 3v₉, at approximately 1289 cm⁻¹, is involved in a strong Coriolis resonance with a dark state near 1301 cm⁻¹, apart from the slightly higher vibrational state v₄. To account for the corresponding Coriolis perturbations as well as the torsional splittings observed in the 3 v₉–v₉ band, a comprehensive line-position fit was performed by simultaneously adjusting three sets of constants for 3v_{9,1}, 3v_{9,2} and the dark state. Accurate rovibrational constants were obtained giving a fit of 947 unperturbed and 146 perturbed lines to rms accuracies of 0.00062 cm⁻¹ and 0.00175 cm⁻¹, respectively. The interacting dark state, found at 1300.7331(19) cm⁻¹, can be assigned to 2v₆ which proves to be responsible for the previously unjustified (A. Perrin *et al.*, *Mol. Phys.* 67, 249–270, 1989) ΔK_c = 6 resonance observed in the strong v₃ band.

Study of Coriolis Coupled v₃ and the Nearby Dark State: The high-resolution infrared spectrum of HNO₃ in the region of 1285–1360 cm⁻¹ has been measured and assigned for the v₃ band. It was found that v₃ at 1326.1856 cm⁻¹ was involved in a strong Coriolis resonance with a dark state near 1343.51 cm⁻¹, apart from the lower bright state v₄. To account for the presently identified Coriolis perturbations, a comprehensive line-position fit of the v₃ band was performed by simultaneously adjusting two sets of spectroscopic constants for v₃ and the dark state v. Optimized rovibrational constants were obtained giving a satisfactory reproduction of most studied transitions. Finally, some weak lines of the dark state band were identified over the spectrum and its integrated band intensity was estimated.

Acetone: Acetone has been identified as a very relevant species in the chemistry of NO_x in the upper atmosphere. Acetone is one of the most abundant carbonyl compounds in the troposphere. It has substantial indirect effects on ozone formation as well as the exchange rate between troposphere and the biological environment. Its abundance is being monitored by several groups with balloon and aircraft flights. The need for accurate values for band intensities was identified during 1997, and we have obtained the first laboratory measurements for about 10 bands of this molecule for temperatures from 230 to 300 K. We used a medium resolution Bruker FTIR instrument at GSFC for these measurements. Two series of spectra were collected from 450 to 1000 cm⁻¹ and 1000 to 3000 cm⁻¹ respectively, using Mylar and KBr beamsplitters in the instrument. Worked on the band intensities in the v₁₉/v₂₃ bands of acetone (CH₃)₂CO) from a low temperature to room temperature. The present results were submitted for publication on 08/24/1999 and accepted on 09/08/1999 by *Spectrochimica Acta Part A..*

New Analysis Tools: Intensity and Broadening Analysis: Allene v_9 and v_{10} . Performed intensity analysis on the v_9 (999 cm^{-1}) and v_{10} (841 cm^{-1}) bands of allene ($\text{H}_2\text{C} = \text{C} = \text{CH}_2$) which is a predicted constituent on titan. We applied some particular high-order dipole-moment terms (derived from the contact transform for asymmetric-top molecules) to a symmetric-top molecule. The formula was further adjusted to the allene molecule according to the symmetry requirements. In fact, very rare papers have been dedicated to line intensity study on such a complicated case: symmetric-top molecule, strong vibration-rotation coupling (l -doubling), strong Coriolis resonance which causes significant intensity borrowing. Studied rotational line broadening of v_{10} (841 cm^{-1}) of allene perturbed by N_2 . This work would help resolve the overlapping lines and account for line wings. Moreover, it will also provide knowledge on allene-nitrogen interacting forces. We again, wrote out the semi-classical forms of a fitting law and a scaling law for a symmetric-top molecule, and applied them to the simulation of the measured N_2 -broadening coefficients. The unique scaling law can deal with the v_9/v_{10} wavefunction mixing arising from Coriolis resonance, an effect that has been seldom touched in previous pressure broadening studies.

Long Path Cryogenic Cell: A new cell with a design pathlength of up to 800 meters has been assembled and tested. Pathlengths of up to 400 meters at 633 nm were achieved. All motors for automated operation and alignment were installed. The vacuum enclosure has been assembled during 1999. We have performed preliminary experiments with the multipass cell looking at two closely spaced lines of water. These lines are assigned to the 454.9850 cm^{-1} line of ground state H_2^{18}O ($9\ 4\ 6 \leftarrow 8\ 1\ 7$) and the 454.9673 cm^{-1} line of H_2^{16}O in the 010 excited state ($8\ 4\ 5 \leftarrow 7\ 1\ 6$). These pure rotational transitions originate from states 879 and 2309 cm^{-1} above zero, respectively. The originally proposed study of water pure rotational spectra in the 300 to 700 cm^{-1} region will follow. We have recently upgraded a Bruker FTIR instrument at Harvard University to operate in the Far-IR. We are currently analyzing water spectra obtained with that instrument and our BIB detectors

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High-Resolution Spectroscopy to Support Atmospheric Measurements

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Research Objectives

Remote sensing experiments on numerous satellite and Space Shuttle missions have shown that space-based measurements of infrared absorption or emission can be used to accurately determine the concentrations and distributions of stratospheric gas species on a global scale. Detailed knowledge of the molecular spectra of ozone and other infrared-active atmospheric species is also needed for accurate calculation of atmospheric heating and cooling rates in climate models. The objective of this research task is to improve knowledge of the infrared spectroscopic line parameters (positions, intensities, assignments, broadening and pressure-induced shift coefficients, and line mixing parameters) of key atmospheric constituents through laboratory measurements. The measurements are made using primarily the McMath-Pierce Fourier transform spectrometer (FTS) facility of the National Solar Observatory on Kitt Peak and the infrared tunable diode laser (TDL) spectrometer at NASA Langley Research Center along with specialized sample cells, many of which were designed and constructed at NASA Langley. Data analysis is performed at Langley Research Center, and the theoretical interpretation of the results is done in collaboration with investigators at several other institutions in the United States and France. These studies have contributed to a number of major upgrades of the HITRAN, GEISA, and other spectroscopic parameters databases with world-wide distribution.

Summary of Progress and Results

We completed our analysis of low-temperature air-broadened and self-broadened ozone spectra in the 4- to 15- μm region recorded with the McMath-Pierce FTS and the NASA Langley coolable cell in 1990 and 1991. Our multi-spectrum nonlinear least-squares technique allowed the determination of pressure-broadening and shift coefficients and their temperature-dependences for numerous ozone lines. These studies resulted in the determination of ozone air-broadening and shift coefficients for nearly 400 previously unmeasured lines in the 9- μm

region and the first determination of these coefficients for ozone in the 13- μm region. In 1997 and 1998 additional spectra were recorded at optimal conditions for determining line broadening and shift parameters in the strong 10- μm band which is most often used for infrared remote sensing of atmospheric ozone. Analysis of these data is in progress.

High-quality low-pressure spectra of pure ozone in the 10- μm region, recorded in 1996 with the McMath-Pierce FTS, have been analyzed to determine absolute intensities for 376 infrared absorption lines with estimated uncertainties of 2 to 5%. An ultraviolet absorption system was used to monitor the ozone amounts in the sample cells, tying the infrared intensities to the ultraviolet absorption cross-section standard at 254 nm. Results compare well with those of researchers from Jet Propulsion Laboratory and two laboratories in France, within the respective experimental uncertainties. This work has recently been submitted for publication.

Extensive studies of broadening, shifts, and line mixing in the 3.3- μm bands of methane (CH_4) are nearing completion. Preliminary data from these spectroscopic studies have been important in the measurements of atmospheric CH_4 and HCl by the Halogen Occultation Experiment (HALOE) instrument currently in orbit on the Upper Atmosphere Research Satellite (UARS). We have now begun similar analyses in the 2.3- μm region used by the MOPITT instrument to be launched on the EOS Terra satellite. In addition, we have analyzed broadening, shift, and line mixing parameters for several bands of monodeuterated methane (CH_3D).

Continuing analyses of other previously recorded spectra has resulted in significant improvement in positions and intensities of carbon dioxide spectral lines in the 2.7- μm region, isotopic ozone lines near 10 μm , and an interacting pair of bands of COF_2 . We have also determined pressure broadening and shift parameters in several CO_2 bands and in the CO fundamental.

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New High-Sensitivity Optical Techniques for Atmospheric Spectroscopy, Kinetics, and Remote Sensing

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Research Objectives

Many trace species of critical importance in atmospheric processes, such as ozone and methane, can be monitored by remote sensing of their absorption and emission bands in the visible to infrared regions of the spectrum. We have been developing several new experimental techniques which provide us with an unprecedented level of sensitivity for trace species, *viz.*, IntraCavity Laser Absorption Spectroscopy (ICLAS) and Frequency-Modulated Differential Absorption Laser (FM-DIAL) spectroscopy. ICLAS, in particular, provides us with a sensitivity equivalent to an atmospheric path length of several thousand kilometers, but in a controlled laboratory environment in which the pressure, temperature, and composition of the sample may be specified and varied at will by the investigator. We have used ICLAS to measure collision-broadening coefficients in the oxygen A band and to acquire and analyze O—H stretching overtone bands in HONO, which have been suggested as a possible source of atmospheric OH radicals. Several improvements to the ICLAS system currently being implemented in our laboratory should significantly increase the accuracy and sensitivity of the method. The FM-DIAL technique, also recently developed in our laboratory, has been shown to have the potential of being a general method for monitoring atmospheric trace gases at ambient levels.

Summary of Progress and Results

ICLAS has been used to measure intensities, N₂-broadening coefficients, and self-broadening coefficients in the A-band ($b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$) of O₂. The broadening coefficients agree to within a few per cent with values measured using long-path multiple-reflection cells by Ritter and Wilkinson [1987] (*J. Mol. Spectrosc.*, 121, 1-19) and more recently by Brown and Plymate [to be published], thereby validating the ICLAS technique for accurate linewidth measurements. New results have been obtained for weakly absorbing transitions, not observed in the earlier

measurements, such as high rotational states (up to $J = 39$), hot-band transitions ($v' = 1 \leftarrow v'' = 1$), and isotopically substituted species ($^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$). Isotopic variants ($^{16}\text{O}_2$, $^{18}\text{O}_2$, and $^{16}\text{O}^{18}\text{O}$) have similar broadening coefficients for corresponding rotational levels, but the self-broadening coefficients are larger in the hot band ($v' = v'' = 1$) as compared with $v' = v'' = 0$ transitions. An ECS-EP scaling analysis of the $v' = v'' = 0$ self broadening data accurately represents the available data, with the exception of the $N = 0$ and $N = 1$ levels.

Recent interest in the study of the overtones of the O—H stretch in HONO has been motivated by the idea that they may be a significant source of photochemical OH production in the upper atmosphere. Using ICLAS, the $3v_{\text{OH}}$ band in HONO has been observed and analyzed, and measurements of the absolute band intensity are being carried out.

Our ICLAS apparatus has recently been improved by implementation of double time correlated sampling and the capability to acquire time-resolved spectra. These improvements, carried out with the assistance of Dr. Alexander Kachanov of UJF Grenoble, significantly increase the sensitivity and measurement accuracy of the method, and allow us to acquire spectra of transient species, e.g., CN radicals resulting from the photolysis of acrylonitrile. We are planning to use time-resolved ICLAS to detect quartet states of NO resulting from energy transfer from metastable Hg atoms; kinetic modeling of the system indicates that ca. 0.1% of the NO molecules should be moved to the $a^4\Pi$ state, which will be readily detectable via the $b^4\Sigma \leftarrow a^4\Pi$ transition in the near-infrared.

Frequency modulation (FM) spectroscopy has been utilized as a high-sensitivity, linear, absorption-based technique for many years. Its capability to reach, in principle, shot noise limited sensitivity has stimulated our interest and promoted our work on developing several new high sensitivity techniques, including FM-DIAL. This is a highly sensitive, pulse-amplified, frequency-modulation based spectroscopic technique for remote sensing applications. We have demonstrated that scattered light returned from a photodetector from distributed scattering centers permits the basic heterodyne detection process to be carried out. The FM photocurrent expected from scattering by an aerosol or cloud is sufficient for detection of atmospheric species over ranges of up to 2 km at levels of 10^6 to 10^{12} molecules cm^{-3} . FM enhanced remote sensing has the potential of being a general method for monitoring atmospheric trace gases at ambient levels.

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Infrared Laboratory Spectroscopy in Support of Stratospheric Measurements

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Research Objectives

The study of laboratory spectroscopy of gaseous molecules, which are important to studies of atmospheric chemistry and dynamics, has been the subject of this program for several years. The molecules investigated include the several isotopic species of water vapor as well as CO₂, N₂O, CH₄, and HNO₃. The information obtained from this task has provided and will provide the atmospheric community with accurate molecular parameters that are necessary for the interpretation of atmospheric data obtained from present (ATMOS and MARK IV) and future (AIRS and TES) experiments. The spectroscopic parameters include vibration-rotation line positions, strengths, air-broadened linewidths and pressure-induced frequency shifts. In some cases the parameters are listed in a compilation which can be easily accessible by interested investigators. One such case is the recently completed compilation of water vapor parameters extending from 500 to 2600 cm⁻¹. This listing contains over 11,000 transitions of H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, HD¹⁶O, and HD¹⁸O.

Summary of Progress and Results

During 1997-1999, several papers were published or submitted for publication (listed below). The results given in the papers involving H₂O and HDO formed the basis from which an extensive compilation of water vapor spectroscopic parameters was generated. This listing covers the region from 500 to 2600 cm⁻¹ and is presently accessible on computer transmission and is presented in HITRAN format. The compilation exceeds any other comparable listing in terms of overall content and accuracy of the parameters. Line strength values of perturbed transitions were computed from results derived from a combination of experimental results with the application of a complete quantum mechanical model. These involved "hot" band transitions with interacting upper states: (020), (100), (001), of H₂O and (020) and (100) of HDO.

Another project was started and completed in 1999. This involved the measurement and analysis of N₂O laboratory spectra. One study involved the determination of line positions and strengths for the region between 3515 and 7800 cm⁻¹ and another included air- and N₂-broadened linewidths and frequency shifts. These investigations compliment earlier studies on N₂O (published by Toth) which covered the region between 900 and 3600 cm⁻¹. A complete and accurate compilation of N₂O parameters from 500 to 7800 cm⁻¹ has been generated from these studies and is presently available to the scientific community.

Also during this period, laboratory spectra of HNO₃ were measured from which line positions and strengths were derived for the 850 to 920 cm⁻¹ region. The input list used in the analysis consisted mainly of the content of the HITRAN compilation which involved over 15,000 lines. The results obtained thus far show that the line strengths of the stronger ground state transitions are about 13% less than those given in the HITRAN listing for this region. The spectra analyzed were of runs with path lengths of 12 cm and sample pressures ranging from 0.16 to 0.34 Torr. The sample temperatures were all 299 K and the spectral resolution was 0.0027 cm⁻¹. Even at this high spectral resolution, the majority of the observed transitions were blended by other HNO₃ lines. Therefore the spectral analysis required computer simulated spectra to match the measured spectra over narrow spectral regions.

Publications

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Laboratory Spectroscopic Measurements Relevant to Upper Atmospheric Research

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Research Objectives

Infrared spectroscopic data, which are needed in remote sensing and global warming studies, are obtained in the laboratory for atmospheric trace gases including C₂F₆, HFC-143a, C₂H₂, N₂O, CO₂, and H₂O. The data are obtained by employing a high-resolution Fourier-transform spectrometer, cryogenically cooled absorption cells at pressures and temperatures representative of the various existing models of the atmosphere and actual conditions recorded in the polar atmospheres, and spectral resolution that is either comparable or is significantly higher than used in many airborne and space-borne missions.

Summary of Progress and Results

We have measured spectral absorption cross-sections in the thermal infrared bands of C₂F₆ and HFC-143a with a Bruker IFS 120-HR Fourier-transform spectrometer and spectral resolution ranging between 0.005 and 0.03 cm⁻¹. The highly accurate cross-section were obtained at temperatures between 180 and 300 K and pressures (of very lean trace-gas-N₂ mixtures) corresponding to the tropospheric and stratospheric layers of all the known model atmospheres and actually monitored in the Arctic and Antarctic atmospheres. The data have been provided to scientists in various remote-sensing missions conducted by United States, Japanese, and European groups. We have also provided the data for inclusion in the future versions of HITRAN and GEISA spectroscopic databases. We have also measured N₂- and air-broadened line widths along with spectral line intensities in the 720 cm⁻¹ band of CO₂, the 13.7 μm band of C₂H₂, and the 6.3 μm band of H₂O. The data obtained at high resolution and low temperatures have been used to validate and improve the existing databases. They have been presented at AGU Fall Meetings, IUGG-99, ASA (Atmospheric Spectroscopic Applications) Conference, ADEOS/ILAS Science Team Meetings, and ASSFTS 8 (8th Atmospheric Science from Space using Fourier Transform Spectrometry), OSA Topical Meetings on Fourier Transform Spectroscopy and on Optical Remote Sensing of the Atmosphere, and the International Spectral Line Shapes Conference that took place during 1997-99. A Ph.D. was awarded to Dr. Vassilii Nemtchinov in August 1998 for work performed during 1994-1998 under this research project.

Publications

None

MODELING AND DATA ANALYSIS

- A. STRATOSPHERIC DYNAMICS AND RELATED ANALYSIS**
- B. ATMOSPHERIC CHEMISTRY ANALYSIS AND RELATED MODELING**
 - B1. PREDOMINANTLY STRATOSPHERIC CHEMISTRY**
 - B2. PREDOMINANTLY TROPOSPHERIC CHEMISTRY**
 - B3. PREDOMINANTLY AEROSOLS AND RADIATION**
- C. GLOBAL CHEMICAL MODELING**

A. STRATOSPHERIC DYNAMICS AND RELATED ANALYSIS



Transport and Mixing in the Stratosphere and Troposphere

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Research Objectives

Long-term changes in the composition of the atmosphere are known to have significant effects on atmospheric chemistry and stratospheric ozone. Increasing levels of greenhouse gases have the potential to change the global climate, in the middle and upper atmospheres as well as in the troposphere. Volcanic eruptions, El Niño events, and other natural variations can also cause changes in atmospheric composition and climate. Whether the causes are natural or manmade, changes in the global climate system can have impacts on human society. In order to understand and predict the consequences of these changes, and of control measures such as the Montreal Protocol, it is necessary to understand the complex interactions between radiation, chemistry, and dynamics in the atmosphere. Much of the uncertainty in our understanding of atmospheric processes comes from an incomplete understanding of atmospheric transport. A complete and self-consistent model of transport requires not only an understanding of trace-species transport, but also the transport of dynamically active quantities such as heat and potential vorticity. Therefore, the goal of the proposed research is to better understand large-scale transport and mixing processes in the middle atmosphere and troposphere.

Summary of Progress and Results

Bowman and Cohen [1997] analyzed a simple model of transport by the Hadley circulation in the tropical troposphere. They found that much of the observed interhemispheric exchange of air could be explained by the seasonal cycle of the Hadley circulation. We are conducting GCM experiments to extend this project to more realistic flows. Our goal is to understand which parts of the global circulation are responsible for interhemispheric tracer transport and mixing in the troposphere. A first step in this study has been submitted for publication [Carrie and Bowman, 1999].

Bowman and Hu [1997] analyzed tropical mixing barriers in the GFDL SKYHI stratospheric general circulation model. The strength of the mixing barriers was found to vary with season and altitude. The applicability of the results to the real atmosphere is limited by the lack of a realistic quasi-biennial oscillation in the version of SKYHI used for this study.

In collaborative work with the Polar Ozone and Aerosol Measurement (POAM) group at Naval Research Lab, Bowman *et al.* [1998] found evidence of potentially serious systematic errors in the global stratospheric analyses produced by NCEP, the UKMO, and the Goddard DAO

analysis systems. The anomalies consist of stationary wave patterns in the summertime stratospheric easterlies, a region from which waves should largely be excluded. Swinbank *et al.* [1999] suggest that improperly assimilated tides are responsible for much of the wavenumber 1 component of the stationary waves. Much of the remaining error may be due to uncorrected biases between different radiosonde types used in different geographic regions. Because the stratospheric data are so important for dynamical and chemical transport studies, it is hoped that these problems will be addressed and corrected in future stratospheric data sets and in reanalyzed data.

Hoppel *et al.* [1999] studied the origins of zonal variability in ozone that occurs during the summer in the Northern-Hemisphere stratosphere. Most of the variability appears to result from stirring by waves in the summer stratospheric easterlies. Wagner and Bowman [1999] carried out a more detailed analysis of the summertime dynamics. They found that the zonal wind profile does filter the wave spectrum, but large-scale stationary and westward-propagating waves do penetrate into the stratospheric easterlies. Although waves in the summer are weak compared to winter, the mean circulation in summer is also weak, so the waves can effectively mix the summer stratosphere. These results support Hoppel *et al.*'s conclusion that transport is largely responsible for the spatial variability of ozone in the summer stratosphere.

We have been developing theoretical models of the dispersion of air parcels in the stratosphere. Statistical analysis shows that air parcel trajectories can be characterized as Lévy flights, which are random walk processes in which the statistics of the random walk have divergent second moments. A manuscript on this subject is currently being revised [Seo, 1999].

Advances in dynamical systems theory, referred to as lobe dynamics, have been shown to have important applications to understanding atmospheric transport. Numerical methods have been developed to apply lobe dynamics theory to real atmospheric flows. With lobe dynamics it is possible to identify mixing barriers and make quantitative transport and mixing calculations. A manuscript containing these results is in preparation [Bowman, 1999].

Publications

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Advanced Methods for Data Assimilation

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Research Objectives

Data assimilation is the process of combining observations of a dynamical system with a computer model of the system, in order to obtain an ongoing best estimate of the evolving state of the system. Increasingly it is being recognized that employing data assimilation methods is likely to play a critical role in furthering scientific understanding of fundamental Earth System processes. While considerable research efforts directed toward the assimilation of meteorological data into atmospheric models have been underway for some time, relatively little attention has been devoted to the assimilation of atmospheric trace constituent data. The behavior of many trace constituents, such as ozone, carbon monoxide, and methane, is vitally important for climate processes. The objective of this research is to carry out a comprehensive study on the assimilation of atmospheric trace constituents, using data primarily from the Upper Atmosphere Research Satellite (UARS), and employing the rigorous, first-principles approach of estimation theory.

Summary of Progress and Results

We have developed a Kalman filter system on massively parallel computers for assimilating limb-sounding observations of stratospheric chemical constituents into a tracer transport model. The system invokes a two-dimensional isentropic approximation, permitting a full Kalman filter implementation and a thorough study of its behavior. Data sets from two UARS instruments with very different viewing geometries, CLAES and HALOE, were used in the assimilation experiments. A robust chi-squared diagnostic, which compares statistics of the observed-minus-forecast residuals with those calculated by the filter algorithm, was used to formulate the statistical inputs to the filter and to validate the assimilation results near the observation

locations. Separate assimilations of the CLAES and HALOE observations were compared to validate the results away from the observation locations. In fact, a wave-breaking event that took place several thousand kilometers away from the HALOE observation locations was well-captured by the Kalman filter due to its highly anisotropic forecast error correlations, and compared favorably against the CLAES assimilation.

Two significant departures from the standard (discrete) Kalman filter formulation were found to be important in this study. Both had a dramatic positive impact on the assimilation results and have altered our path on the quest to advance the state of the art of data assimilation. First, it was discovered that the standard Kalman filter covariance propagation is unacceptably inaccurate for trace constituent assimilation. Spurious and rapid loss of variance and increase of correlation length scales occur as a result of diffusion of the small-scale structures inherent in tracer error covariance fields. A new formulation based on well-understood properties of the continuum error covariance propagation was therefore introduced. Second, validation diagnostics suggested that the initial error, model error, and representativeness error are all more appropriately assumed to be relative than absolute for trace constituents. A filter formulation for relative errors was therefore devised.

With these two modifications, it was possible to make an assessment of the relative importance of the various components of the Kalman filter assimilation system, and therefore to open up further avenues toward advancing the state of the art of data assimilation. In particular, it was found that the primary contributor to optimality of a tracer assimilation system is evolving the error correlation, which can create analysis increments that extend the influence of the observations far away from the observation locations.

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Dynamical Meteorology of the Tropical and Extratropical Stratosphere

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Research Objectives

An observational study of the dynamical meteorology of the equatorial and extratropical stratosphere was performed, emphasizing large-scale motions and their coupling with the underlying troposphere.

Summary of Progress and Results

The quasi-biennial oscillation (QBO) was simulated in one- and two-dimensional models calibrated to reproduce approximately the observed magnitude and vertical structure of Brewer-Dobson upwelling in the equatorial lower stratosphere. The role of intermediate and small-scale gravity waves was emphasized as a source of vertical transport of horizontal momentum in addition to that of large-scale, long-period Kelvin and Rossby-gravity waves. Data from the UARS Halogen Occultation Experiment were used to refine previous estimates of vertical mean motion, vertical diffusivity, and lateral in-mixing. Also studied were various effects of the QBO including a modulation of the overlying stratopause semiannual oscillation, interannual variation of the extratropical winter middle atmosphere in both hemispheres, and isentropic tracer transport due to breaking planetary Rossby waves. The QBO is not the only source of interannual variability in northern winter; also important are variations attributable to the Arctic Oscillation (AO) and planetary-wave activity originating in the troposphere. It was shown that the warm phase of the AO is related to polar stratospheric warming events. In both phases, the signature of the AO propagates downward from the mid- to lower stratosphere. In winter the tropospheric component of AO coincides approximately with the arrival of a downward-propagating stratospheric AO anomaly near the tropopause. Studies are in progress on (1) the propagation of low-frequency Rossby wavetrains from the troposphere to lower stratosphere; (2) principal components of stratospheric zonally averaged circulation and long-lived trace constituents, using UKMO and HALOE data; (3) observations of inertia-gravity waves and inertial instability near the tropospheric jetstream, using MU radar data and high-resolution rawinsondes, in collaboration with Dr. Kaoru Sato; and (4) evidence of Kelvin waves and tropical intraseasonal oscillations (TIO) in water vapor from the UARS Microwave Limb Sounder. Comparison of the TIO signal in the upper troposphere and tropopause region suggests that the water vapor response in the moist phase of the TIO undergoes a phase reversal between

the two levels, consistent with our hypothesis that deep convection moistens the upper troposphere but also causes an elevated tropopause with reduced water vapor in the immediate vicinity of the tropopause. It remains to be determined whether the drying observed in the 100 hPa satellite retrieval is attributable to a reduced saturation mixing ratio at the tropopause, anomalous upwelling of dry tropopause air, or some combination thereof.

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Parameterization of Gravity Wave Variability for Chemical and Microphysical Models

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Research Objectives

Gravity waves are medium scale motions that produce important synoptic-scale effects in the stratosphere. Since these motions are not resolved in global models, their effects must be parameterized. Recently it has become clear that gravity wave temperature perturbations significantly affect stratospheric microphysics and chemistry, yet existing gravity wave parameterizations do not model these effects. The aim of this project is to provide a suite of new gravity wave parameterizations specifically designed for chemical and microphysical applications, which can be easily incorporated into global chemical transport models (CTMs) and general circulation models (GCMs). We seek realistic parameterizations not just of occasional "bursts" of wave activity from strong sources, but also statistical parameterizations of the background levels of gravity wave activity routinely found in the stratosphere. These parameterizations will be tested in CTM and GCM studies, and "benchmarked" against measurements of stratospheric gravity wave events, such as those encountered by the National Aeronautics and Space Administration (NASA) stratospheric ER-2 research aircraft.

Summary of Progress and Results

Our approach to the task has been to parameterize two types of gravity wave activity that we view as being sufficiently distinct to require separate parameterizations.

The first type of gravity wave activity we have parameterized is the ambient background fluctuations that are present much of the time in the stratosphere. Observations have shown that these perturbations consist of a pseudo-random spectrum of many interacting waves, but that the

power spectral densities have a reproducible form. We have adopted a simple model of these gravity wave spectra, and extended it to provide spectra of wave-induced temperature and heating/cooling rate perturbations. We also developed an algorithm to convert these spectra into time series of Lagrangian temperature perturbations experienced by a parcel, and tested it using a box trajectory model of stratospheric microphysics [Bacmeister *et al.*, 1999]. The parameterization appears to work well, and is ideal for use in global CTM studies.

It was unclear how best to model gravity wave-induced perturbations of trace species: global stratospheric studies have used parcel advection methods, whereas mesospheric gravity wave studies used Eulerian perturbation methods instead. Both methods were formalized and interrelated by Eckermann *et al.* [1998], and shown to be largely similar. Parcel advection is preferable for the highly structured minor species profiles and cloud patterns often encountered in the stratosphere. This method can also model gravity wave spectra [Eckermann, 1999].

The second type of gravity wave activity we have parameterized is mountain waves. Our approach has been to upgrade significantly the NRL Mountain Wave Forecast Model (MWFM), which was originally designed to forecast mountain wave-induced turbulence for the ER-2. Many new features have been included in the MWFM for chemical and microphysical applications. Some of the more important are realistic density stratification effects, nonhydrostatic three-dimensional ray-tracing of waves, a mesoscale temperature and cloud supersaturation prediction capability, and generalizations to three-dimensional mountains. These MWFM predictions compare well with stratospheric mountain waves measured by aircraft [Eckermann and Marks, 1997] and from satellites [Eckermann and Preusse, 1999]. We now have two working MWFM models: the enhanced operational model (MWFM) and a significantly enhanced next generation model (MWFM 2.0), the latter currently being extensively tested and refined in a research capacity.

These new capabilities have enabled the MWFM to model a number of mountain wave-induced polar stratospheric clouds (PSCs) occurrences in the Arctic [see, e.g., Carslaw *et al.*, 1998b; Rivière *et al.*, 1999]. Use of MWFM in a CTM showed solid PSC particles penetrating long distances downstream of the mountain wave formation regions [Carslaw *et al.*, 1999]. Global MWFM CTM simulations led Carslaw *et al.* [1998a] to suggest that mountain wave-induced PSCs may deplete overall levels of Arctic ozone during winter. In the winter of 1999-2000, NASA will conduct the airborne SAGE III Ozone Loss and Validation Experiment (SOLVE) out of Kiruna, Sweden, to study this and many other issues related to Arctic ozone. We will use the MWFM during SOLVE as both an in-field turbulence forecast tool for the ER-2 and a research tool for modeling mountain wave effects on stratospheric microphysics and chemistry.

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Climatological and Dynamical Studies with SAGE Data

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Research Objectives

Scientific investigations were carried out into the nature of the stratospheric circulation by analyzing data products from the SAGE II satellite experiment. This work also involved applying the University of Wisconsin 2-D WISCAR and 3-D non-hydrostatic models. It was found to be beneficial to undertake a relatively complete analysis of ECMWF data to define seasonal regional structures relevant to constituent distributions. Specifically, we focussed on: (1) analysis of seasonal patterns of significant zonal asymmetries, including the monsoon structures of the tropical lower stratosphere, the Aleutian High during the northern winter, and the "South African High" during the southern winter; (2) analysis of ER2 data, ECMWF data, and SAGE constituents to better understand the nature of constituent gradients in the subtropics; (3) employing the WISCAR 2-D model to investigate the role of source/sink patterns and transport in explaining observed constituent distributions; and (4) employing the University of Wisconsin non-hydrostatic model in conjunction with aircraft campaign data to better understand synoptic to mesoscale circulations affecting constituent distributions.

Summary of Progress and Results

Seasonal Zonal Asymmetries: Our most significant result is the discovery that stratosphere-troposphere exchange across the subtropical tropopause occurs primarily in the summertime and over the oceans, downstream of the climatological monsoon anticyclones [Postel and Hitchman, 1998]. As travelling synoptic waves propagate along the subtropical westerly jet, they interact with the divergent outflow from monsoon tops, resulting in pronounced geographical maxima in Rossby wave breaking downstream over the summer oceans. The climate implications of this are manifold. Stratospheric air is chronically advected into the tropical upper troposphere equatorward of the monsoon highs, altering the chemical and radiative properties of the vast tropical upper troposphere. At the same time, tropospheric air readily enters the extratropical lower stratosphere in these surf zones, modifying the chemical environment of stratospheric ozone. These seasonal Rossby wave breaking maxima in the upper troposphere and lower stratosphere can help explain a variety of phenomena, including the "lower transport regime," the "substratosphere," tracer correlation diagrams, and a double peak in age of air recently identified by Arlyn Andrews. These mixing zones thus constitute useful mental models and may be useful in guiding future aircraft/satellite measurement campaigns.

Median values of SAGE II (1984-94) and SAM II (1979-94) aerosol in bins 30 degrees longitude \times 5 degrees latitude \times 1 km were calculated. These climatological aerosol distributions are very useful in illustrating preferred pathways of constituent exchange with the tropics. During the northern winter a preferred pathway is found emanating from near the Amazon High, spiraling across Africa, over East Asia, and into the Aleutian High. This air of tropical origin has low potential vorticity and high aerosol. This work has been reported in publications [Harvey and Hitchman, 1996; Hitchman *et al.*, 1997; Harvey *et al.*, 1999] below.

Subtropical Stratospheric Fronts: We find that the subtropical region of enhanced constituent gradients coincides with enhanced PV gradient, but that this has been widely misinterpreted as a “transport barrier.” ER-2 data support the idea that active mixing occurs across these air mass boundaries, or fronts, which are in fact produced by differential advection in the large-scale flow associated with Rossby wave breaking.

2-D Modeling: The WISCAR model now runs on a local workstation, has useful QBO [Politowicz and Hitchman, 1997] and aerosol parameterizations, and has been used in model intercomparisons and age-of-air studies.

Modeling Transport with the UW-NMS for Aircraft Campaigns: We have carried out a simulation of the central Pacific region during the ASHOE/MAESA campaign of March 1994. Idealized tracers were initialized with a view toward understanding how convective complexes might contribute toward the observed vertical structure of aerosol and water vapor near the tropopause. Realistic 3-D gravity waves are generated by the model convection which affect idealized constituent distributions.

Our work for POLARIS has shown that the seasonal change in net transport likely accounts for a significant portion of the column ozone loss experienced during each northern summer. Hitchman *et al.* [1999] describes analysis of ER-2, balloon, satellite, UW-NMS calculations with idealized tracers, box model estimates, and a derivation of the Stokes’ drift expected from synoptic waves in the lower stratosphere. Upwardly-evanescent synoptic waves transport ozone downward in the lower stratosphere all year, but the import of ozone from the tropics ceases going into northern summer, yielding a net ozone transport out of the stratosphere.

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Wave Dynamics and Transport in the Stratosphere

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Research Objectives

This grant supports a program of theoretical studies, numerical modeling, and data analysis designed to elucidate the dynamics of motions in the stratosphere and their role in the transport of heat, momentum, and trace chemical substances in the lower stratosphere, and across the tropopause. The emphasis of the project is on the physics of gravity wave motions generated by convection in the troposphere, and the role of interactions between gravity waves and the large-scale flow in maintaining the observed heat, momentum, and trace species budgets in the stratosphere.

Summary of Progress and Results

Gravity Wave Modeling: A two-dimensional cloud-resolving model was used to examine the possible role of gravity waves generated by a simulated tropical squall line in forcing the quasi-biennial oscillation (QBO) of the zonal winds in the equatorial stratosphere. A simulation with constant background stratospheric winds was compared to simulations with background winds characteristic of the observed westerly and easterly QBO phases. The magnitude of zonal forcing induced by this wave damping was of order $5 \text{ m s}^{-1} \text{ day}^{-1}$. It was estimated that if 2% of the area of the tropics were occupied by storms of similar magnitude, mesoscale gravity waves could provide nearly 1/4 of the zonal forcing required for the QBO.

Gravity Wave Climatology: We applied a linear gravity wave propagation model together with observations of the background wind and stability fields to compute climatologies of gravity wave activity for comparison to observations. This work did not lead to the expected constraints for parameterizations because it was found that quantitative comparisons between observations and the model depend sensitively on the strength and intermittency in gravity wave sources, properties which are largely unknown. Instead the results led to some new interpretations of existing observational studies of the climatology of gravity wave activity. It was found that globally and seasonally uniform gravity wave sources input to the model can reproduce many of the seasonal and geographical trends seen in data from both satellite (UARS Microwave Limb

Sounder) and rocket-based platforms. Previous interpretations of the observed climatology have instead often emphasized the importance of seasonal and geographical variations in gravity wave sources for explaining the wave activity variations.

Observations in the lower stratosphere from radiosondes were found to be more sensitive to true variations in gravity wave sources than were the satellite and rocket observations. The results of this model comparison also suggest some new ways to analyze and report observations that can yield useful constraints for gravity wave parameterizations in the future.

Satellite Observations of Gravity Waves: Horizontal temperature variances derived from optically-thick radiance measurements from the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS) were used as a proxy for gravity wave activity in the stratosphere and lower mesosphere. Six years of data, which include both limb-scanning and limb-tracking measurements, provides information for horizontal length scales ranging from 30 to 1000 km. A careful examination of the horizontal and vertical scale-sensitivity of MLS was made and the resulting three-dimensional response functions were used in the interpretation of the results. Seasonal climatologies exhibited regions of large variance at high latitudes in the winter hemisphere and distinct maxima in the subtropics over the continental landmasses in the summer hemisphere. Attention was focused on the summertime maxima since these are unlikely to be a result of filtering effects by background mean winds. A gravity wave ray-tracing model that employs background mean winds for the same period as the MLS was used as an interpretive tool. The model results reveal that mean wind effects are not responsible for the longitudinal variation of the summertime subtropical maxima. Furthermore the model was also able to simulate the variance patterns for the different viewing geometries of MLS. Finally, a comparison of the MLS results to maps of cloud top temperatures shows a good correspondence in the summer-time subtropics providing evidence that an important source of these waves is deep convection.

Tracer Filamentation: Vertical soundings of stratospheric ozone often exhibit laminated tracer structures characterized by strong vertical tracer gradients. The change in time of these gradients was used to define a tracer lamination rate. It was shown that this quantity is given by the cross product of the horizontal temperature gradient and the horizontal tracer gradient. Climatologies based on UARS ozone data and temperatures and on an ozone-like pseudo tracer (based on modified potential vorticity) were computed. Three stratospheric regions with high lamination production rates were found: the stratospheric overworld near the edge of the polar vortex, the lowermost stratosphere in the vicinity of isentropes crossing the tropopause, and in the subtropical lower stratosphere. Seasonal variations, and contrasts between the Northern and Southern Hemispheres were explored.

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TOMS Validation Using ER-2 and Ground-Based Datasets

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Research Objectives

The primary goal of our research effort for NASA's Atmospheric Chemistry Modeling and Analysis Program (ACMAP) is to use data collected during the 1997 NASA-sponsored Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) field campaign for the validation of Total Ozone Mapping Spectrometer (TOMS) total ozone and tropospheric ozone retrieval algorithms, specifically under conditions of high solar zenith angles and high latitudes. Data obtained during POLARIS from ground-based instruments (Dobson spectrometer, Brewer spectroradiometer, and the JPL MkIV infrared interferometer) and ECC ozonesondes were compared with the Earth Probe and ADEOS TOMS data sets.

Summary of Progress and Results

Accurate, traceable ozone column measurements are an essential cornerstone on which to base studies of photochemical and dynamical changes in total ozone. Before summertime ozone loss at high northern latitudes can be explained, the pattern of ozone loss must first be quantified. This pattern of seasonal ozone loss over Fairbanks, Alaska was investigated during the NASA POLARIS campaign in the spring and summer of 1997. Five independent data sets of total ozone observations at Fairbanks were compared, from the Earth Probe and ADEOS Total Ozone Mapping Spectrometer (TOMS) satellite instruments, balloon-borne electrochemical concentration cell ozonesondes, and ground-based (Brewer spectroradiometer, Dobson spectrophotometer, and the Jet Propulsion Laboratory MkIV infrared interferometer) instruments. The excellent agreement between different observational techniques lends confidence to the observed rate of summertime loss of total ozone at high latitudes.

The five POLARIS total ozone data sets agree remarkably well in magnitude, forming an envelope with a standard deviation relative to either EP TOMS or the Brewer on the order of 10 DU. Over the 6 months of data considered, ADEOS TOMS satellite measurements are about 7 DU higher than EP TOMS, which is higher by about 8 DU than the Brewer; the MkIV interferometer lies in the middle between EP TOMS and the Brewer; the Brewer agrees

remarkably well (within 1 DU) with the Dobson; and the sondes using the 0.5% KI cathode solution measure about 7-10 DU less than the Brewer. Ranking in order of magnitude, ADEOS TOMS > EP TOMS > MkIV > Brewer \approx Dobson > Sondes (SBUV) \approx Sondes (CMR). In relative terms, the highest (EP TOMS) and lowest (ozonesondes) ozone values measured over the entire 6-month period agree to within 5%. The fact that the MkIV, which is an infrared instrument, falls between the TOMS and Brewer/Dobson measurements (which all employ UV techniques) suggests that there is no apparent bias between the IR and UV cross sections of ozone employed by these instruments. The observed small offsets between the different measurement techniques are consistent with our current understanding. All observations show a seasonal, summertime ozone loss of about 30 DU per month between April and August, with minor dynamically induced oscillations in total ozone with a period of about 2 weeks and an amplitude of about 40 DU superimposed on the general decline.

The positive offset of EP TOMS relative to the Brewer (9.3 ± 9.3 DU, 1 standard deviation) and Dobson (9.6 ± 9.3 DU, 1 standard deviation) instruments is consistent with comparisons made by the TOMS retrieval team at NASA Goddard Space Flight Center (GSFC) between EP TOMS and several other high-latitude ground stations (positive offsets of up to 3%). For the time period of August 1996 to April 1998, EP TOMS showed a positive bias against the Dobson at Fairbanks of 2.65% with a standard deviation of 3.61%. When ADEOS TOMS was compared to the same Dobson instrument for the period September 1996 to June 1997, the offset and standard deviation were 3.90% and 2.75%, respectively. While the source of this offset is unknown, it is consistent with differences between Nimbus 7 TOMS (reprocessed with the version 7 TOMS algorithm) and 30 Northern Hemisphere Dobson stations, in which the average difference between TOMS and the Dobson stations increases as a function of total column ozone, up to almost 3% at 500 DU. Since total ozone is typically higher at high latitudes, this may indicate a possible issue with the TOMS retrieval algorithm at high latitudes.

Another possible source of disagreement between the TOMS and ground-based observations is the fact that the Dobson instruments are routinely intercompared and calibrated at locations where the total ozone is much lower than 500 DU. The response at high ozone values varies from instrument to instrument when compared to TOMS.

Standard deviations between EP TOMS and all the other instruments during POLARIS are 9-11 DU (about 3%). When the local gradient in overhead ozone is large, the noncoincidence in time of the TOMS and ground-based observations of several hours can easily lead to discrepancies of more than 10 DU. The noncoincidence of data during periods of a large gradient in overhead ozone can be seen to produce an enhancement in the standard deviation by artificially shifting the time of the EP TOMS observations by one day. While this does not change the absolute offset between the TOMS and Dobson observations (9.6 DU) for the entire POLARIS campaign, it more than doubles the standard deviation (from 9.3 DU to 20.2 DU).

Publications

Lloyd, S., W. H. Swartz, T. Kusterer, D. Anderson, C. T. McElroy, C. Midwinter, R. Hall, K. Nassim, D. Jaffe, W. Simpson, J. Kelley, D. Griffin, D. Nicks, B. Johnson, R. Evans, D. Quincy, S. Oltmans, P. Newman, R. McPeters, G. Labow, L. Moy, C. Seftor, G. Toon, B. Sen, and J.-F. Blavier, Intercomparison of total ozone observations at Fairbanks, Alaska during POLARIS, *J. Geophys. Res.*, 104, 26767-26778, 1999.

General Circulation of the Southern Hemisphere Stratosphere

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Research Objectives

This project focuses on the dynamical processes at work during the seasonal evolution of the southern stratosphere and the reasons for the interhemispheric differences in the stratospheric circulation.

Summary of Progress and Results

Simulation of the Stratospheric Circulation with a GCM: The sensitivity of the stratospheric circulation simulated by an atmospheric general circulation model (the UCLA AGCM) to modifications in the parameterizations of several key physical processes has been investigated. For this work, we focused on the Northern Hemisphere winter season. The effect of different ozone mixing ratios was first examined by comparing multi-year simulations with distributions of ozone mixing ratio that were either prescribed according to an observed climatology or predicted using a formulation of photochemical processes. The prescribed ozone mixing ratios produced a considerably more realistic circulation. To address some remaining difficulties, we took a closer look into the radiation parameterization. This led to adjustments to radiative cooling rates in the upper stratosphere, and to the finding that the simulation of the polar night jet is very sensitive to these adjustments. These results confirm that the performance of an AGCM in the stratosphere can depend on several different model aspects, and that this dependence is not always straightforward. We also argued that the results of these experiments support the notion that parameterizations of orographic gravity wave drag that neglect or underestimate the drag in the troposphere may overestimate the drag in the stratosphere.

The performance of the UCLA AGCM's simulation of the stratospheric circulation has been compared with that of other contemporary GCMs as part of the GCM-Reality Intercomparison Project for SPARC (GRIPS).

Transport Processes in the Southern Polar Stratosphere: In preparation for STRATEOLE, we examined transport processes in connection with ozone variability in the wintertime Southern Hemisphere polar lower stratosphere. Chemistry in this region is such that ozone is mainly conserved on time scales of a few days, with sparse and localized chemical sources and sinks. The winter polar vortex strongly controls transport in the polar regions and dynamic processes

can be approximately reconstructed by advecting air parcels along isentropic surfaces. We have analyzed in detail the ozone evolution in the lower stratosphere during the period August 5-10, 1994. The emphasis was on the ozone "collar" (the band of maximum values in ozone mixing ratio around the Antarctic ozone "hole") and the development of "collar filaments." Ozone mixing ratios provided by the Microwave Limb Sounder (MLS) and by an ER-2 aircraft participating in the ASHOE/MAESA campaign were compared with values at corresponding locations in high-resolution maps obtained by using the numerical scheme of Contour Advection with Surgery (CAS). The CAS-reconstructed ozone maps provide a view of the way in which air masses are exported from the outskirts of the collar to form the "tongues" of higher mixing ratios observed at lower latitudes on MLS-synoptic maps. There is an overall consistency between the data sets insofar as the collar location is concerned, which seems to be primarily defined by the local properties of the flow. The CAS-reconstructed collar tends to be weaker than that depicted by MLS data. By means of radiative calculation estimates, we argued that diabatic descent may be responsible for maintaining the ozone concentration approximately constant in the collar while filaments isentropically disperse collar-like mixing ratios from this region towards lower latitudes.

Variations in the Stratospheric Circulation: Our previous results obtained using a primitive equation model of the middle atmosphere showed there can be substantial interannual variability in the stratospheric winds and wave amplitudes during the late winter and spring seasons under these conditions. To gain a better understanding of the mechanisms producing the interannual variations in these simulations, we have been using a highly-truncated quasi-geostrophic model on a beta plane. The interannual variations in stratospheric planetary wave amplitudes and zonal mean zonal wind in the presence of steady planetary waves in the troposphere have been examined through an analysis of the steady solutions of the model as well as time integrations. The model can include the interactions of the zonal mean flow with planetary waves as well as the interactions of these waves with each other, and is thus an extension of that used in Yoden [1987]. Using this model, Yoden [1990] did not find any interannual variations when the lower boundary forcing is constant in time. We also found no interannual variations are found if the flow is forced to a radiative equilibrium condition that is annually-periodic with a radiative damping time of ~20 days in the lower stratosphere, the value used in Yoden [1990]. We have demonstrated that interannual variations can be obtained during winter and spring in this model if two requirements are met. First, the radiative damping time is doubled in the lower stratosphere to a value in closer agreement with observational estimates. Second, if the model's truncation includes the anti-symmetric mode about the channel center. The two requirements complement each other in the following way. Larger radiative damping times imply that the system can "remember" different conditions at the beginning of the previous summer, when otherwise the system memory is lost. Non-symmetric conditions about the channel center imply that the mean zonal winds in early winter do not have a critical level across the entire domain. It is also demonstrated that interannual variations can be obtained for shorter system memories by considering the stochastic effect of synoptic-scale transients. These results suggest that a rich variety of variations in the stratospheric circulation are possible even under constant 'external' conditions.

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Temperature Trends from Satellite Data

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Research Objectives

The goal of this task is to utilize the various NCEP analyses, the NCEP/NCAR reanalysis, GSFC GEOS-STRAT assimilation data, SBUV and TOMS ozone data, and the GSFC 3-D chemistry/transport model to better understand both trace gas distributions, variability of the stratosphere, and the processes which control the dynamics of the stratosphere.

Summary of Progress and Results

Twenty-one years of NCEP CPC analyses, 40 years of NCEP/NCAR re-analyses, 8 years of UKMO data, and 4 years for GEOS-STRAT analyses are currently available to the GSFC user community via the mass data storage system at GSFC, and via magnetic disk drives on the local Code 916 machines. These analyses are current to date, via an automatic updating system which has been implemented between GSFC and NCEP. A storage format has been developed for the transparent distribution of the data to a heterogeneous spectrum of computer systems, including users external to GSFC. We currently use an automated e-mailing system to distribute maps and data to users worldwide. An on-line meteorological Atlas is regularly updated on the World Wide Web (see http://hyperion.gsfc.nasa.gov/Data_services/met/nmc_climatology.html).

The data have been utilized to study the 1996 Southern Hemisphere ozone hole, have been used to analyze the 1996-1997 Northern Hemisphere winter ozone distribution, and the polar vortex breakdown during the winter of 1997. Current work is focussed on understanding the quantitative relationship between the wave driving of the stratosphere by planetary waves originating in the troposphere.

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Convectively Generated Gravity Waves

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Research Objectives

The goal of this project is to understand and quantify the importance of mesoscale convectively generated gravity waves to the tropical stratospheric momentum budget. Included in this is an examination of the nature of the gravity waves generated by convection, as revealed by aircraft measurements. This study is motivated by clear observational evidence from aircraft and radars of significant amplitude gravity waves above tropical convective systems the fact that planetary scale waves alone cannot account for either the stratopause semiannual zonal wind oscillation or the lower stratosphere quasi-biennial zonal wind oscillation.

Summary of Progress and Results

We have devoted most of the effort for FY97 and 98 (funding ended with FY98, but work is continuing) to carefully evaluating the waves generated by a particular convective system observed during the STRAT campaign in late 1995 in the mid-Pacific. We have been able to identify several distinct quasi-monochromatic waves over this convective system. These include: 1) waves with horizontal wavelengths of about 50 km and vertical wavelengths of 5-10 km; 2) waves with horizontal wavelengths of about 8 km that are vertically propagating; and 3) waves with horizontal wavelengths of about 4 km that are vertically trapped (as expected by theory). On this basis, we have filtered the data to include only vertically propagating waves and calculated momentum fluxes. We have found momentum fluxes consistent with expectations in that momentum fluxes are directed away from the convective system. However, the magnitudes are quite small compared to those found in a monsoon system analyzed by a colleague and myself in 1995. Moreover, it appears that most of the momentum flux is NOT due to the quasi-monochromatic waves analyzed for this system. The implications and significance of this finding are currently being evaluated. One thing that is clearly pointed to by these results, however, is that far more measurements of stratospheric mesoscale gravity waves generated by convection are needed to fully evaluate their significance for driving the tropical stratospheric circulation. We clearly do not have enough measurements to know how much momentum flux comes from a convective system. In the meantime, the monochromatic wave results are being readied for submission to a journal in the next few months.

Publications

None

Analysis of Aircraft and Satellite Measurements of Lower Stratospheric Trace Gases and Lagrangian Photochemical Modeling

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Research Objectives

This Atmospheric Chemistry Modeling and Analysis Program (ACMAP) research involves the integration of long-term global satellite observations, *in situ* high resolution aircraft measurements, and Lagrangian photochemical calculations designed to improve our observational characterization and theoretical understanding of lower and middle stratospheric chemistry and transport. Satellite observations provide a global, long-term perspective for the interpretation of *in situ* data sets while *in situ* measurements provide a stringent test of the ability of satellite retrievals to characterize instantaneous atmospheric variability. The Langley Research Center (LaRC) Lagrangian photochemical model developed under this proposal provides a means of blending these measurements in a physically consistent manner, and also provides an opportunity to assess our current understanding of the photochemical and dynamical processes which determine the distribution of trace species in the Earth's atmosphere. Part of this research included participation in the 1997 Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) campaign. During POLARIS, satellite observations of ozone and key species involved in summer time polar ozone loss (namely NO_x) by the Halogen Occultation Experiment (HALOE) onboard the Upper Atmospheric Research Satellite (UARS) were used to initialize the LaRC Lagrangian photochemical model which, in conjunction with assimilated wind and temperature fields, was used to predict the photochemical evolution of airmasses observed by HALOE.

Summary of Progress and Results

- LaRC Lagrangian photochemical predictions during POLARIS show large-scale ozone loss in high latitudes at ER2 flight altitudes of over 10% per month in June and July, in good agreement with photochemical calculations based on ER-2 observations. Largest

summertime losses (over 2.6 ppmv/month) are found to occur poleward of 60N above 30 mb, in good agreement with photochemical calculations based on Mark IV observations. Analysis of photochemical and residual transport tendencies showed that they tend to be of similar magnitude but opposite sign. Photochemical loss of ozone tends to outweigh positive transport tendencies in high latitudes, while upwelling of low ozone below the tropical ozone maximum moderates photochemical production there.

- A new sub-grid-scale mixing parameterization for use in Lagrangian trajectory studies was developed. LaRC photochemical model predictions of O₃ and CH₄ were compared with *in situ* measurements made from the ER-2 platform during POLARIS. Comparisons made in April 1997 show that irreversible mixing was important in establishing observed tracer-tracer correlations during spring 1997. Comparisons made in late June 1997 indicate that remnants of air from the polar vortex survived unmixed in the low stratosphere 6 weeks after the breakup of the polar vortex in May.
- In late March 1997 HALOE observed very low ozone (less than 1 ppmv at 480K), low HCl, high NO_x within the Arctic polar vortex. Trajectory mapping techniques were used to show that the lower stratospheric Arctic vortex was chemically perturbed, but not dehydrated during this period. Correlations of ozone, water vapor, NO_x, and HCl with HF were used to quantify the changes in these constituents during the period. Temporal changes in the correlation of HCl and NO_x with HF indicate increases in these species during March and early April 1997. No trend in the correlations of water vapor or ozone with HF was found during March and early April in the lower stratosphere.
- Stratospheric aerosol profiles at high northern latitudes from the Stratospheric Aerosol Measurement (SAM) II experiment were used to show that tropical, aerosol rich air tends to accumulate in the Aleutian High from 15 to above 30 km, and in the North Atlantic High in the 15-25 km layer. A trajectory case study was used to investigate the hypothesis that the observed aerosol maxima are maintained by episodic poleward surges of high aerosol air from the tropical stratospheric reservoir.
- A method for evaluating the seasonal evolution of ozone laminae using ozonesonde data was developed. The method uses the correlation between small-scale ozone and potential temperature variations to distinguish between laminae generated by quasi-isentropic filamentation by Rossby waves and by vertical displacements of material surfaces by gravity waves. Data from Wallops Island, Virginia show that Rossby wave induced ozone laminae are most frequently encountered at Wallops during the winter months near 15km while statistically significant gravity wave induced laminae occur above 15km during the early winter and at the tropopause from late winter through early spring.

Publications

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Large-Scale Stratospheric Transport Processes

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Research Objectives

This is a wide-ranging project covering many aspects of the large-scale dynamics of the stratosphere and of the theory of stratospheric transport. The greatest emphasis is on the development of theoretical ideas required to interpret observations of stratospheric chemical constituents and meteorology, and the results of chemical transport models.

Summary of Progress and Results

Dynamics of the Brewer-Dobson Circulation and Tropical Upwelling: Although it has in the past been common to regard the stratospheric circulation as being “driven” by diabatic heating and cooling, it is now recognized that global scale, axisymmetric, circulations of this kind cannot exist without some kind of drag acting on the flow. Consideration of the angular momentum budget led to the concepts of the “extratropical pump” and “downward control.” However, these principles cannot explain the tropical Brewer-Dobson circulation in terms of extratropical “pumping.”

Using a two-dimensional dynamical model, we have made calculations of the circulation driven by mid-latitude wave drag. For this model, it is found that, if the wave drag is confined to latitudes greater than about 20 deg from the equator, there is little equatorward penetration of the meridional circulation. If the region of wave drag is shifted further equatorward, however, the (more realistic) circulation extends across the equator, and there is substantial upwelling at and around the equator.

Circulations may also be driven by small latitudinal gradients of thermal forcing—both tropospheric and stratospheric—within the tropics. However, we found that it takes both mid-latitude wave drag and tropical thermal forcing to produce a realistic seasonal cycle of tropical upwelling.

This work is described in Plumb and Eluszkiewicz [1999].

Quantifying and Modeling Stratospheric Transport: There have been several recent studies aimed at putting numbers on quantities such as “the transport out of the polar vortices” and “transport across the tropopause.” Several of these numbers appear to be mutually contradictory, even when the same meteorological data sets have been used. Part of the problem, we believe, is

conceptual: there is implicit disagreement about what “the transport out of the polar vortices” really means (e.g., precisely how does one define the boundary across which transport is to be evaluated?).

Use of Lagrangian techniques to define “the” boundary provides more robust answers. When a filament is drawn off the polar vortex, transport is considered to occur only when the filament has been thinned to such an extent that molecular diffusion (or perhaps small-scale mixing, depending on the viewpoint) become active. Once the filament has been stretched below some specified (small) scale, transport is irreversible (i.e., it is then inevitable that the filament will become mixed eventually). Thus, transport is quantified through an inventory of the mass being stretched into filamentary structures. These structures are identified in reverse domain filling (RDF) calculations using a technique we refer to as “local gradient reversal,” which is analogous to contour surgery, but can be applied to gridded data.

This work is described in detail in Sobel *et al.* [1997], and in Adam Sobel’s Ph.D. thesis [Sobel, 1997].

The Dynamics of the Diabatic Circulation---Non-Zonally Averaged Theory: We have used an approach based on the PV-coordinate theory of Nakamura to investigate the dynamics of the polar vortex based on “vortex-following” coordinates. We have completed the shallow water case, in which a height-field relaxation is imposed as an analog of diabatic heating. Hence, we have shown that in the climatological steady state in which the mass contained within a given PV contour is constant (though the contour itself may be wobbling arbitrarily), the net “diabatic heating” within the contour is nonzero only if frictional effects are active on the contour (and thus, in practice, only if the wave is breaking at that contour). Thus, diabatic dissipation of the wave motions cannot drive “descent” within the vortex in a shallow water model.

This work is described in Adam Sobel’s Ph.D. thesis [Sobel, 1997] and in Sobel and Plumb [1999]. We are currently extending this work to the 3-D case.

The Structure of Stratospheric “Age.” We have used a simple “leaky pipe” model of the stratosphere to investigate the processes that control the distribution of “age.” We have shown that the tropics-to-mid-latitude age difference at any altitude is determined only by the net tropical upwelling rate at that altitude, and is independent of any recycling of air between tropics and extratropics. The effect of any such recycling is to make the air older everywhere.

This work is described in Neu and Plumb [1999].

The Effects of Mixing on Tracer Relationships in the Arctic Vortex: Tracer-tracer relationships have been found to be robust characteristics of the extratropical stratosphere. Occasionally, especially in the polar vortices, anomalous relationships are observed. These have been interpreted as indicative of denitrification and of chemical ozone loss; however, data from the ATMOS instrument in the Arctic vortex have shown similar anomalies for passive species for which sedimentation or chemical loss is out of the question. Using 2-D and 3-D models, we have shown that such anomalous relationships can be explained as resulting from the mixing of air across the vortex edge.

This work is described in Plumb *et al.* [1999].

Models and Measurements II: We were involved in the design of transport experiments as part of the Models and Measurements II exercise, and in analysis of the results from transport experiments. This work is included in the Models and Measurements II report [1999] and results from the "age" experiments are described in Hall *et al.* [1999].

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Trace Gas Transport in the Troposphere

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Research Objectives

This project is aimed at understanding the “big picture” of tropospheric transport, and has two main focuses: assessment of the robustness and significance of tracer-tracer relationships in the troposphere, and investigation of the nature of tracer transport in mid-latitude baroclinic systems, including near-surface transport associated with frontal systems.

Summary of Progress and Results

Tracer Relationships: We have investigated tracer relationships in a chemical transport model (CTM), and in surface data. The model results show that, for two long-lived tracers with Northern Hemisphere sources, the tracer-tracer relationship is compact in the Southern Hemisphere and in the tropics, and that its slope is in agreement with the ratio of net sources. This agrees with theoretical predictions. Preliminary analysis of ALE/GAGE/AGAGE data from Tasmania and Samoa seems to show consistency with this result; however, the precision of the data limits how well this statement can be made for many species pairs of interest over synoptic time scales. (This analysis is continuing.) We are also planning further CTM experiments with an updated model.

Transport by Baroclinic Eddies: Work thus far on this project has been focused on model development and on the design of appropriate experiments. We are using a global, primitive equation, pseudo-spectral dynamical atmospheric model to simulate the statistical equilibrium of a simple but unstable basic state. We have now completed such an experiment and have just begun analysis of its transport properties.

Publications

None

Studies of Interannual Stratospheric Variability Related to Global Change

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Research Objectives

Our objectives are to use long records of satellite constituent measurements, together with global stratospheric meteorological analyses, to quantify and understand seasonal and interannual variability in constituent and dynamical (transport) fields. Our focus has been on quantifying the global seasonal variation of stratospheric ozone, NO_x, H₂O and CH₄, together with interannual variability due to long term trends, the 11-year solar cycle, the quasi-biennial oscillation (QBO), and the El Chichon and Pinatubo volcanic eruptions. We also search for coupling between the troposphere and stratosphere on seasonal and interannual time scales, as evidenced in dynamical and constituent observations.

Summary of Progress and Results

Seasonal Cycle of Stratospheric Water Vapor: We have studied the seasonal variation of H₂O and CH₄ in the stratosphere based on HALOE measurements. The global budget of stratospheric CH₄ has been analyzed based on the transformed Eulerian-mean formulation, quantifying the roles of mean and eddy transports in the middle and upper stratosphere. We have used SAGE II H₂O measurements to quantify the seasonal variation of H₂O in the extratropical lowermost stratosphere (the ‘middleworld’), and used these results to infer the importance of isentropic versus diabatic transport to maintain the observed distributions.

Stratospheric Constituent Trends: We have used SAGE I/II data to quantify decadal trends in stratospheric ozone and NO₂ (although the NO₂ results await further reprocessing of the SAGE II data). We also performed trend analyses of the relatively short HALOE CH₄ and H₂O data sets, finding intriguing changes (increases in H₂O and negative CH₄ trends) during the first several years of HALOE (~1991-1995). However, these data show relatively small trends after 1995, so that the early changes may be episodic in character.

Temperature and Dynamic Variability and Trends: Global temperature variability was analyzed based on stratospheric sounding unit (SSU) and MSU observations for 1978-1998 (together with NCEP and UKMO data). We have quantified large cooling trends in the springtime polar region of both hemispheres since 1978, and shown a strong space-time coherence with observed ozone trends. We have also quantified the global dynamical structure of the quasi-biennial oscillation

(QBO) based on UKMO and SSU data sets (together with HALOE constituents). Our results provided novel details of the QBO effects on the residual mean meridional circulation, and highlighted QBO variability in the upper stratosphere and in extratropics. We have also collaborated with Darryn Waugh (Johns Hopkins University) to use 'elliptical diagnostics' to analyze the climatology and interannual variability of the NH and SH stratospheric polar vortices, and quantify variability in vortex persistence in spring.

Tropospheric Constituent Transport: Together with a Ph.D. student (Beth Stone), we quantified the global transport of constituents in the troposphere associated with baroclinic waves. This work was based on studying idealized baroclinic wave life cycles using the NCAR CCM2, which included several passive tracers. Results showed that constituents are systematically adverted upwards and polewards by the tropospheric circulation, with transport predominantly due to the eddy fields.

Contribution to Assessments: We contributed lead authorship for the SPARC 1998 Assessment of Trends in the Vertical Distribution of Ozone, and to the 1999 WMO Ozone Trends Assessment. Current work includes contribution to the SPARC Water Vapor Assessment.

Publications

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Acquisition of Near-Tropopause Meteorological Data from Commercial Aircraft

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Research Objectives

By capturing observations from the flight data recorders of commercial aircraft, we obtain extensive information in exactly those areas (near the tropopause, near major air corridors) where key aspects of trace constituent chemistry and dynamics need study. Further, by obtaining information from more than 57 aircraft per day continuously since 1996, we complement the many field experiments which can obtain more sophisticated dynamical and chemical measurements, but can only occur on a relatively expensive, field-campaign basis.

Summary of Progress and Results

During the period of this grant, we compared the subtropical observations with current generation analyses and also demonstrated that the aircraft can show discrepancies with the tropical meridional flows making up the Hadley circulation. We published one paper on the aircraft results and prepared a second one for submittal.

One significant problem with chemical trajectory models is that the greatest dispersion occurs near the strong jets whose actual strengths and shears are most questionable. In the absence of other information, chemical transport studies use the results of operational analyses or reanalyses to specify these winds. But our previous work has shown that such analyses are in error ranging from 11-17% in the early 1990s to 5-8% in the mid 1990s [Tenenbaum 1991, 1996; Rukhovets *et al.*, 1998]. Because the high-resolution aircraft data has been collected continuously since August 1996, we have begun to validate the most current models (~50 km resolution for the European Centre for Medium Range Weather Forecasts, ECMWF; lesser resolutions for other national centers). Such models still show the weak wind bias even when the aircraft data is averaged onto the grid spacing of the assimilation models (<http://purvid.purchase.edu/cases/98011400.gif>).

A separate physical process affecting chemical transport models is the overall accuracy of the mean meridional tropical flow (the Hadley circulation). By using the aircraft observations in the tropics, we were able to show that the moisture parameterizations which dominate such flows were also inaccurate. These results, presented at the 2nd International Reanalysis Conference [Tenenbaum, 1999] were confirmed by other studies [Arpe and Rhodin, 1999]. It is widely agreed that the meridional flows are dominated by the moist convective parameterization in a

region where observational data is already sparse. By obtaining high-resolution wind observations that are independent of any assimilation system, we are able to provide a clear test of the parameterizations at multiple widely separated longitudes. As we pursue the implications of the apparent subtropical barrier to the free exchange of chemical species, such inaccuracies in the meridional flow make it difficult to disentangle the underlying mechanisms.

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Transport and Mixing in the Stratosphere and Troposphere from Chemical Tracer Measurements

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Research Objectives

The objective of this study is to determine what aspects of the transport and mixing within the stratosphere and troposphere can be inferred from measurements of trace constituents. Using chemical transport models we will test various diagnostics used to extract information about the transport and mixing from tracer measurements. By sampling the tracer distribution from the model in the same manner as observations and comparing estimated transport diagnostics with more precise measures, derived from simulations of idealized tracers or from other model diagnostics, we will identify uncertainties and biases in the different analysis techniques. The initial focus will be on existing analysis techniques, but subsequent work will examine new methods for extracting transport information from tracer measurements. We will consider not only previous measurements but also proposed (or hypothetical) measurements; this will provide guidance on what measurements will be best for inferring various aspects of the circulation. As well as assessing what aspects of the circulation can be inferred from chemical tracer distributions we will also use available measurements to infer characteristics of the transport in the real atmosphere, and perform some model-model and model-data comparisons. Circulation characteristics to be examined include transport between the tropical and extra-tropical stratosphere, mixing of vortex air into middle latitudes, and transport from the troposphere into the stratosphere.

Summary of Progress and Results

Three (collaborative) studies have been completed under this project.

As part of the NASA "Models and Measurements II" study, we evaluated the transport characteristics of two- and three-dimensional chemical transport models of the stratosphere by comparing their simulations of the mean age of stratospheric air and the propagation of annually periodic oscillations in tracer mixing ratio at the tropical tropopause into the stratosphere to inferences from *in situ* and satellite observations of CO₂, SF₆, and water vapor. The models display a wide range of performance. Most models propagate annual oscillations too rapidly in the vertical, and overattenuate the signal, and also significantly underestimate mean age throughout the stratosphere. In the lower stratosphere, model-to-model variation in N₂O, NO_y, and Cl_y is well correlated with variation in mean age, and the magnitude of NO_y and Cl_y variation

is large. We conclude that model transport inaccuracies significantly affect simulations of important long-lived chemical species in the lower stratosphere.

Following on from the above study, we explored the sensitivity of the mean age to different components of the transport by examining the effect of varying the transport parameters within a two-dimensional model. The mean age is shown to be sensitive to changes in advective circulation and diffusion coefficients, with the sensitivity being largest for changes in the circulation strength. In most cases the magnitude but not the orientation of the mean age isopleths change. However, if the horizontal mixing is made very small within middle latitudes or large within low latitudes large changes occur in the orientation of mean age isopleths. The effects of these transport changes on chemically-active long-lived tracers are also examined. It is found that the lower stratospheric concentrations are relatively insensitive to the transport changes if these changes do not alter the general shape of mean age isopleths. However, significant changes occur when the transport parameters are modified so as to change the orientation of the mean age (and chemical tracer) isopleths. These results provide useful information on what the mean age distribution (from observations or models) tells us about the different components of stratospheric transport (in real or model atmosphere).

In recent years several studies have used observed tracer-tracer relations to quantify chemical processes, in particular chemical ozone loss and denitrification, occurring within the polar vortices. However, in such calculations it is assumed that the tracer relations are not affected by mixing and that the observed change is due totally to anomalous chemistry. In collaboration with Drs. Alan Plumb and Martyn Chipperfield, an examination of the effects of mixing on vortex tracer relations has been performed by analyzing observations and results from a simple model and three-dimensional chemical transport models. Observations from several different platforms, and from different winters, show changes in the vortex relationship between long-lived tracers that are transport induced (as there is no conceivable chemical explanation). Furthermore, analysis of model simulations show similar anomalous tracer-tracer relations due to mixing, and that this mixing occurs continuously rather than in single event. This analysis suggest that if tracer relationships are to be used to quantify ozone loss or denitrification then the changes due to mixing need to be taken into account, and that simple mixing line arguments are unlikely to work.

Publications

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Dynamical Coupling of the Troposphere With the Polar Stratosphere

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Research Objectives

The objective of this project is to examine the variability of the dynamical and thermal structure of the wintertime Arctic lower stratosphere, and its coupling with the tropospheric circulation. The primary focus is on the aspects that potentially play an important role in the depletion of stratospheric ozone, especially regions of very low temperatures and their relationship with the polar vortex. The orientation of the thermal patterns relative to the polar vortex determines the flow through the coldest air masses, which can strongly influence the extent of chemical processing. Therefore, the dynamical and thermal structure of the stratosphere will be examined from a vortex-oriented perspective. Simultaneously, the structure and variability of the tropospheric circulation will be analyzed (by a variety of diagnostics), and the relationship between different stratospheric and tropospheric flow regimes examined. The analysis will be performed using both meteorological analyses and results from climate model simulations. The analysis of observations will define a vortex-oriented climatology of the winter stratosphere (including intraseasonal, interannual and decadal variability), while comparisons of the climate models with the observations will assess how well these models reproduce the lower stratospheric structure, and its coupling with troposphere.

Summary of Progress and Results

The persistence of the Arctic and Antarctic lower stratospheric vortices has been examined over the period 1958 to 1999. Three different vortex-following diagnostics (two using potential vorticity and one based solely on the zonal winds) were compared, and shown to give very similar results for the break up date. The variability in the timing of the breakup of both vortices is qualitatively the same: there are large interannual variations together with smaller decadal-scale variations and there is a significant increase in the persistence since the mid-1980s (all variations are larger for the Arctic vortex). Also, in both hemispheres there is a high correlation between the persistence and the strength and coldness of the spring vortex, with all quantities having the same interannual and decadal variability. However, there is no such correlation between the persistence and the characteristics of the mid-winter vortex. In the Northern Hemisphere there is also a high correlation between the vortex persistence and the upper tropospheric/lower stratospheric eddy heat flux averaged over the two months prior to the

breakup. This indicates that the variability in the wave activity entering the stratosphere over late-winter to early-spring plays a key role in the variability of the Arctic vortex persistence (and spring polar temperatures) on both interannual and decadal time scales. However, the extreme values of Arctic vortex coldness and persistence during the 1990s are not echoed as similar extreme in the eddy heat flux. This suggests that the recent increase in vortex persistence is not due solely to changes in the wave activity entering the stratosphere.

Publications

Waugh, D. W., W. J. Randel, S. Pawson, P. A. Newman, and E. R. Nash, Persistence of the lower stratospheric polar vortices, *J. Geophys. Res.*, to appear, 1999.

**B. ATMOSPHERIC CHEMISTRY ANALYSIS AND RELATED
MODELING**

- B1. PREDOMINANTLY STRATOSPHERIC CHEMISTRY**
- B2. PREDOMINANTLY TROPOSPHERIC CHEMISTRY**
- B3. PREDOMINANTLY AEROSOLS AND RADIATION**



B 1. PREDOMINANTLY STRATOSPHERIC CHEMISTRY



Use of POAM III Data in the SOLVE Campaign

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Research Objectives

The NRL Polar Ozone and Aerosol Measurement (POAM III) is a currently operational visible/near infrared solar occultation instrument in a polar orbit aboard the SPOT 4 spacecraft. The objective of this research task is to use POAM III in the SOLVE campaign. This participation will include, first of all, validation of the SAGE III data. POAM III is uniquely important for Meteor 3M SAGE III validation because they are in similar orbits. Thus, many validation opportunities occur during the course of a year. Also, POAM III measures the same constituents as SAGE III (in the solar occultation mode), and uses the same measurement technique and wavelength range. Thus, fundamental measurements (slant optical depths), as well as geophysical retrievals, can be compared. The second major objective of the task is to participate on-site during the SOLVE field campaigns, and make the POAM III data available on a daily basis to the SOLVE science team. This is important because during the ER-2 deployments centered around 21 February, SAGE III measurements will occur about 10 degrees poleward of the POAM III measurements. Thus, the sampling of the vortex provided by SAGE III and POAM III during this time is likely to be different. Therefore, with regard to SOLVE, SAGE III and POAM III are complementary and both will provide valuable information for flight planning and science activities. Finally, we will infer ozone loss for the 1999-2000 winter using the POAM III data and the REPROBUS CTM (Chemical-Transport Model), and make detailed comparisons with the results obtained in the SOLVE measurement/model investigations.

Summary of Progress and Results

This is a new program with initial funding received in June 1999. We have participated in the initial SOLVE planning meeting held in January 1999. A computer to be used for POAM data analysis and display at the SOLVE field site in Kiruna has been purchased. We have provided POAM measurement ephemeris information for the SOLVE time frame to other SOLVE Investigators. Also, in order for POAM to be useful in flight planning and data interpretation, an important issue is the time required for availability of the POAM data. Therefore, over the past several months, much emphasis has been placed on this issue. We have developed, and are presently testing, a plan which will allow the POAM data to be processed and made available to researchers in Kiruna within about 24 hours of data acquisition. Of particular interest is the POAM polar stratospheric cloud (PSC) detection algorithm. The operational PSC algorithm is not real-time, but rather requires data for an entire season before detection statistics are compiled. This algorithm has now been modified for real-time operation, and the results are being evaluated and compared with those from the operational algorithm. Finally, we have developed several POAM data display and plotting algorithms to be used at the field site in Kiruna.

Publications

None

Satellite-Based Stratospheric and Tropospheric Measurements: Determination of Global Ozone and Other Trace Species

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Research Objectives

This program is designed to (a) refine the measurement capability for satellite-based instruments that monitor ozone and other trace species in the Earth's stratosphere and troposphere, and (b) to retrieve global distributions of these and other constituents (clouds and aerosols) from the GOME and SCIAMACHY satellite instruments. Trace gases retrieved include BrO, OCIO, SO₂, H₂CO, NO₂, H₂O, CO, N₂O, CH₄, and CO.

Ozone profiles are determined from inversion of the back scattered light intensity measured between 250 and 350 nm in a manner similar to that used by the SBUV/TOMS instruments. Additional information from the high-resolution observation of the temperature-dependent Huggins bands is used to help distinguish tropospheric from stratospheric ozone, while the visible Chappuis bands are employed to constrain the total ozone column.

Summary of Progress and Results

The research at the SAO for the GOME and SCIAMACHY projects includes development and maintenance of scientific software for the GOME retrieval algorithms, advising and assisting in the development of GOME operational software, participation in GOME validation and science studies, sensitivity and instrument studies to help finalize the definition of the SCIAMACHY instrument (now completed), development of scientific software for SCIAMACHY retrievals, and consultation on the development of NRT and OL operational data processing and data products.

One of the major research efforts has been the development of a linearized discrete ordinate radiative transfer code (LIDORT) for retrieval and forward model studies in inhomogeneous scattering atmospheres. In this work, the full multiple scatter backscatter intensity solution has been subject to an internal perturbation analysis, thus allowing the model to generate whole

fields of weighting functions simultaneously. This is a vital requirement for non-linear iterative retrieval algorithms; the generic formalism of LIDORT will enable it to be used in a wide variety of remote sensing problems. Work has started on a vectorized version of LIDORT for the Stokes-vector treatment of polarized light. The application of LIDORT to GOME and SCIAMACHY is direct and immediate. One of the most important uses will be for the performance enhancement of the ozone profile retrieval algorithm for both instruments. This will go a long way to the realization of an operational O₃ profile retrieval algorithm for GOME; work toward this goal has started.

An additional major research effort has been the continued improvement of trace gas fitting. This is based on the substantial background work that we have developed in spectrum fitting, instrument calibration and characterization, reference spectrum improvement, and Ring effect determination. SAO determined a method for correcting GOME data for spectral undersampling and developed several methods for wavelength calibration of GOME spectra using a Fraunhofer reference spectrum (in collaboration with colleagues at ESA and DLR). BrO retrieval studies continue, including: (1) cross-validation among the different groups fitting GOME data, where the SAO fitting has been shown to be the most precise; (2) comparison of BrO and cloud fields to examine the tropospheric content of BrO. Preliminary determinations indicate that there is not a substantial, several pptv background of BrO in the lower troposphere. Work is currently in progress to further quantify this conclusion (see below). Research done in conjunction with our NASA ACMAP grant has allowed us to determine H₂CO from GOME in stable fashion, for the first time (preliminary studies, by the DLR and SAO allowed measurements of high pollution episodes). We are currently investigating the development and distribution of H₂CO emissions from the Amazon biomass burning. SO₂ fitting studies are currently underway; volcanic SO₂ is routinely measured, and we expect to be able to measure SO₂ from anthropogenic pollution to high precision within several months.

The method of determining height-resolved ozone from nadir measurements proposed by SAO has now been successfully implemented by several research groups, including Rutherford Appleton Laboratory and the University of Bremen, and KNMI and SRON in the Netherlands. The current difficulty is the requirement for substantial computation time in retrieval of profiles; they require several orders of magnitude over real time. SAO has furnished an operational framework and prototype to the DLR for future use. SAO is currently developing real-time profile capability.

SAO has now completed development of CRAG (the Cloud Retrieval Algorithm for GOME) for operational implementation by DLR, and maintains a scientific version for additional studies. One of the first of these, currently underway, is the comparison of BrO column measurements with cloud fields over the tropical Pacific in September 1998, to quantify the BrO residual below cloud top height. Preliminary SAO studies have given upper limits of 0.3-0.5 pptv BrO below 500 mbar.

SAO has participated in the development of extended capabilities for the HITRAN database, including the addition or extension of UV/visible spectra of O₃, OCIO, BrO, H₂CO, ClO, NO₂, O₂, NO, and OH.

Publications

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Modelling of Cloud Microphysics, Heterogeneous Chemistry, and Photochemistry for the SAGE III Ozone Loss and Validation Experiment (SOLVE)

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Research Objectives

We will be providing modelling products in support of the SOLVE campaign, primarily using a trajectory model with detailed microphysics, heterogeneous chemistry, and gas-phase chemistry. The primary objectives are to compare the ability of competing polar stratospheric cloud (PSC) theories to match SOLVE measurements, evaluate different heterogeneous reactions and their parameterizations, and examine the sensitivity of ozone depletion to these parameters. Simulations will be done of each ER-2 flight and of all DC-8 and balloon encounters with PSCs, gravity wave events, or cirrus clouds. Modelling will focus on products that can be directly compared to observations, with quantitative comparisons of various model scenarios to determine which are best able to match the data. Post-mission analyses will explore the evolution of the whole Arctic vortex during the 1999-2000 winter, in particular to examine chlorine evolution and ozone depletion.

Summary of Progress and Results

The only objective of this project in FY99 has been to prepare for the SAGE III Ozone Loss and Validation Experiment, which will take place during the 1999-2000 winter. Towards that end, we have purchased and configured a new computer to take into the field and have upgraded existing equipment. We have improved the computer models that will be used to analyse the measurement data. We have participated in mission planning, attending the planning meeting in January, and providing preliminary model output to the project scientists to assist in designing flight paths.

Publications

None

Modeling of the Partitioning of Reactive Odd Nitrogen in the Lower Stratosphere Using Aircraft Measurements of NO_y, NO, and Other Species

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Research Objectives

The suite of simultaneous measurements available on the ER-2 includes a wide variety of long-lived and reactive species. The time and location of measurements includes periods in all seasons, altitudes in the upper troposphere and lower stratosphere, and a wide latitude range in both hemispheres. The goal of this task is to use these ER-2 observations and models to address the distribution and partitioning within the NO_y reservoir, the controlling photochemical and transport processes, and the interaction of the NO_y reservoir with other reactive species. Included in this effort are local steady state, trajectory, full diurnal photochemical, and two-dimensional models.

Summary of Progress and Results

Interpretive efforts in this period focussed on data from the 1997 Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) and earlier missions.

Del Negro *et al.* [1999] make use of stratospheric measurements of NO, NO₂, O₃, ClO, and HO₂ that were made during spring, early summer, and late summer in the Arctic region during 1997 as part of the POLARIS field campaign. In the sunlit atmosphere, NO₂ and NO are in steady state through NO₂ photolysis and reactions involving O₃, ClO, BrO, and HO₂. By combining observations of O₃, ClO, and HO₂, observed and modeled values of the NO₂ photolysis rate coefficient (J_{NO_2}), and model estimates of BrO, several comparisons are made between steady state and measured values of both NO₂ and J_{NO_2} . An apparent seasonal dependence in discrepancies between calculated and measured values was found; however, a source for this dependence could not be identified. Overall, the mean linear fits in the various comparisons show agreement within 19%, well within the combined uncertainties (± 50 to 70%). These results suggest that photochemistry controlling the NO₂/NO abundance ratio is well represented throughout much of the sunlit lower stratosphere. A reduction in the uncertainty of laboratory determinations of the rate coefficient of $NO + O_3 \rightarrow NO_2 + O_2$ would aid future analyses of these or similar atmospheric observations.

In Gao *et al.* [1999], use is made of extensive airborne measurements of the reactive nitrogen reservoir (NO_y) and its component nitric oxide (NO) made in the lower stratosphere during POLARIS. Box model simulations that are constrained by observations of radical and long-lived species and which include heterogeneous chemistry systematically underpredict the NO_x (= NO + NO_2) to NO_y ratio. The model agreement is substantially improved if newly measured rate constants for the OH + HNO_3 and OH + NO_2 reactions are used. When included in 2-D models, the new rate coefficients significantly increase the calculated ozone loss due to NO_x and modestly change the calculated ozone abundances in the lower stratosphere. Ozone changes associated with the emissions of a fleet of supersonic aircraft are also altered.

Keim *et al.* [1999] extend recent studies which used NO, NO_y , OH and HO_2 (HO_x) observations and which postulated that acetone and convection of peroxides are significant sources of HO_x in the upper troposphere (UT). The new work focuses on the effect these additional HO_x sources have on the modeled NO_y partitioning and comparisons of the modeled NO_x/NO_y ratio to observations. The measured NO_x/NO_y ratio is usually much higher than predicted regardless of the presence of acetone in the model. The exception occurs for air parcels having low NO_y and O_3 values. For these air parcels the measured NO_x/NO_y ratio is much lower than the calculated ratio unless acetone is included in the model. In all cases acetone increases the fraction of NO_y that is peroxyacetyl nitrate (PAN) from typical values of much less than 0.1 to values as high as 0.35. Including acetone also reduces the scatter in a comparison between modeled and observed NO_x/NO_y ratios.

In Gao *et al.* [1998], *in situ* measurements in the engine exhaust of a Concorde supersonic aircraft in the lower stratosphere are used to constrain heterogeneous reaction rates on soot particles in a plume model. Upper limit values are obtained for the product of the reactive uptake coefficients of O_3 and NO_2 and the mean surface area of individual soot particles by using the model and the well-established $\text{O}_3\text{-N}_2\text{O}$ correlation in the lower stratosphere. The low reactivity value obtained for O_3 implies that soot reactions cannot account for ozone trends in the lower stratosphere.

In Gao *et al.* [1997], use was made of the measurements of nitric oxide (NO), nitrogen dioxide (NO_2), and total reactive nitrogen ($\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HNO}_3 + \text{ClONO}_2 + 2\text{N}_2\text{O}_5 + \dots$) made during austral fall, winter, and spring 1994 as part of the NASA Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft mission. Comparisons between measured NO_2 values and those calculated using a steady-state (SS) approximation are presented for flights at mid- and high latitudes. The SS results agree with the measurements to within 8%, suggesting that the kinetic rate coefficients and calculated NO_2 photolysis rate used in the SS approximation are reasonably accurate for conditions in the lower stratosphere. However, NO_2 values observed in the Concorde exhaust plume were significantly less than SS values. Calculated NO_2 photolysis rates showed good agreement with values inferred from solar flux measurements, indicating a strong self-consistency in our understanding of UV radiation transmission in the lower stratosphere. Model comparisons using a full-diurnal, photochemical steady-state model also show good agreement with the NO and NO_2 measurements, suggesting that the reactions effecting the partitioning of the NO_y reservoir are well-understood in the lower stratosphere.

Publications

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Algorithm for Future Ozone Profiling Using Limb Scatter Measurements

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Research Objectives

The aim of this research is to develop a retrieval algorithm for stratospheric ozone profiles using spaced based limb scatter measurements. This method should have vertical resolution of 1-3 km (much better than the current Solar Backscatter Ultra Violet method of 8-15 km) and global coverage (more than that the 30 measurements per day of the Stratospheric Aerosol and Gas Experiment). It is hoped that such a measurement technique will help in understanding such questions as what are the ozone temporal trends in the lower stratosphere. This technique will be used by several new instruments, such as the Optical Spectrograph and Infrared Imaging System (OSIRIS), the Scanning Imaging Absorption SpectroMeter for Atmospheric ChartographY (SCIAMACHY), and the Ozone Mapping/Profiler Suite aboard the National Polar-orbiting Operational Environmental Satellite System (OMPS/NPOESS), to monitor O₃ well into the 21st century.

Summary of Progress and Results

An algorithm for ozone profiling using measurements of ultra violet (UV) and visible light scattered from the earth's limb was written and tested. This was used to investigate the sensitivity of the retrieval to the assumptions employed. Theoretical calculations show that in the upper stratosphere the pointing of the instrument is the largest source of error and is correlated with the scale height of the ozone profile. The assumed temperature profile is also important due to the resulting uncertainty in the ozone absorption cross section, but this can be minimized with an appropriate choice of wavelength pairs having similar sensitivities to temperature. In the lower stratosphere, the scattering of light by stratospheric aerosols can greatly affect the limb scattered radiance, but the effect upon the retrieval is reduced significantly by taking measurements on both sides of the Chappuis absorption band centered at 600 nm.

Scattering by clouds below the line of sight is not a significant source of error in the case of homogeneous cloud fields. Heterogeneous or broken cloud fields, however, do present more of a problem. Preliminary simulations show that some cloud patterns can cause as much as 7% error at km. Much more work must be done in the theoretical area of this problem to better understand the implications.

Furthermore, this algorithm was used to analyze data taken during the Shuttle Ozone Limb Sounding Experiment/Limb Ozone Retrieval Experiment (SOLSE/LORE), which flew in early December 1997. The results from this mission proved to be quite successful and are the first to demonstrate that limb scattering measurements in the UV and visible wavelength regions can be used to retrieve the profile of ozone in the upper and lower stratosphere regions (50-15 km). Comparisons with balloon sondes taken on the same day and data from HALOE on the next day are generally within at least 20% of the SOLSE/LORE retrievals. Analysis of the flight data for a couple of cloudy scenes did not show errors due to broken cloud fields. More flight data is needed to confirm this.

In March 1999, the SCIAMACHY Science Advisory Group (SSAG) Meeting was attended in SRON/Utrecht, NL to assess the capabilities of SCIAMACHY limb scatter measurements. This should prove to be a valuable source of data for further validation of this method, however, ESA's work on the retrieval algorithm had yet to begin.

Manuscripts are in preparation for a detailed error analysis of the retrieval algorithm used with the SOLSE/LORE data, an error analysis of the RSAS pointing technique and the radiative transfer model used. Much of the current research effort is directed toward gaining a better understanding of the effect of broken cloud scenes, and a means of mitigating any errors. The effects of horizontal variations in the ozone profile will also be examined, and it is hoped that lessons learned from the MLS-2/EOS-CHEM science team can be applied to the limb scatter technique. We are continuing our close contact with personal from the Integrated Program Office (IPO) and its OOAT, which provides Government scientific oversight of OMPS. Knowledge gained in our research is being passed onto NASA in a very timely fashion, so that advice NASA provides the IPO will go toward ensuring the success of OMPS.

Publications

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Satellite Data Studies of the Middle Atmosphere

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Research Objectives

Our primary objective is to apply existing long-term satellite remote-sensing measurements to better define the sources of interannual stratospheric ozone change, with emphasis on components associated with tropospheric climate change and solar variability. Specific tasks include: (i) empirical estimates of dynamical contributions to column ozone trends at northern mid-latitudes; (ii) observational estimates of the solar component of long-term stratospheric ozone variability; and (iii) theoretical investigations of physical mechanisms involved in climatic and solar forcing of long-term ozone variability in the stratosphere.

Summary of Progress and Results

Several efforts were made to quantify the contribution of climate-driven trends in stratospheric circulation to column ozone trends at northern mid-latitudes. Most recently, the contribution of trends in the rate of eddy transport across the subtropical tropopause to the column ozone trend in the lowermost stratosphere was estimated. The procedure involved calculating trends in Ertel's potential vorticity on the 330 K potential temperature surface as a function of latitude and longitude in the Northern Hemisphere for the months of February and March over the 1979 to 1998 period. These trends were found to be generally negative at northern mid-latitudes, reflecting increased transport of tropical upper tropospheric air into the mid-latitude, lowermost stratosphere. Regression relationships between 330 K PV and total ozone deviations derived from monthly mean measurements on the northern hemisphere were then applied to estimate that as much as 40% of the zonal mean total ozone decline at mid-latitudes in February during the analysis period was attributable to long-term trends in eddy transport. As much as 25% of the trend in March was attributable to the same source.

The eddy induced ozone trend was interpreted to imply an increased occurrence of anticyclonic, poleward, Rossby wave breaking events that transport ozone-poor air across the subtropical tropopause into the mid-latitude, lower stratosphere. According to independent research by others, the latter type of breaking event is favored when the background zonal wind field is either anticyclonic or weakly cyclonic. Statistical trend analyses of NCEP gradient zonal winds for the months of February and March demonstrated that the mid-latitude wind shear has tended to become less cyclonic with time over the analysis period. This reflects a tendency for a stronger winter polar vortex in most of the 1990s as compared to the 1980s. Since the period of analysis

covered only 20 years, it is not yet clear whether the stronger polar vortex is a temporary climatic deviation or is part of a long-term trend.

The characteristics of the quasi-decadal oscillation of the upper and lower stratosphere have been determined further via statistical analyses of extended data sets covering the 1979 to 1998 period. The upper stratospheric (1-2 mbar) ozone variation from solar minimum to maximum is in the range of 2.5-4.5% while current stratospheric models that account for observed changes in solar ultraviolet flux predict corresponding ozone variations of only 0.5-2.0%. In contrast, the observed solar cycle ozone variation in the middle stratosphere (5-10 mbar) is in the range of 0-1.5% while the corresponding model prediction is 2.0-2.5%. The difference in the upper stratosphere was interpreted to imply that transport-related changes in the concentrations of key trace constituents that determine the ozone catalytic loss rate may be occurring between solar minimum and maximum during the analysis period. Statistical analyses of temperature profile records for the same time period are consistent with increased upwelling in the tropical middle stratosphere at solar maximum relative to solar minimum. Increased upwelling at these levels would increase the upper stratospheric abundance of transportable trace constituents, including methane, which would increase the ozone abundance at solar maximum. Such an expectation may be consistent with observed decreases in upper stratospheric methane from 1992 and 1996, with a partial recovery thereafter. Increased upwelling in the tropical middle stratosphere, where the ozone lifetime is comparable to dynamical transport time scales, may also produce transport-related ozone decreases at solar maximum, which could be consistent with the reduced ozone solar response at these levels. A test of this provisional interpretation will be possible if methane observations are continued through the approaching solar maximum.

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Three-Dimensional and Trajectory Chemistry-Transport Modeling for SOLVE

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Research Objectives

The objective of this work is participation on the mission theory team for the SAGE III Ozone Loss and Validation Experiment (SOLVE). We will support the SOLVE mission by contributing: (1) results from the Goddard global three-dimensional model of stratospheric chemistry and transport; (2) calculations of chemistry along back trajectories from the aircraft and balloon flight tracks; and (3) expert analysis for mission planning, flight forecasting, and data interpretation. These contributions continue along the lines of our work in previous aircraft missions. Deliverables and applications are provided in collaboration with SOLVE mission management and the entire science team. We are focussed on the science issues of simulating observed ozone loss, modeling rates of heterogeneous processes including particle formation and chlorine activation, deactivation of chlorine following cold temperatures, evaluating observational techniques for estimating ozone loss, validation of SAGE III measurements, and effects of aircraft traffic in the upper troposphere and lower stratosphere in winter.

Summary of Progress and Results

Progress and results from this effort are measured from the beginning of the project in 1999. The major activity is expected to come in the year 2000 during the SOLVE field deployment and afterward in analysis of the data. Progress to date has been made on three fronts.

First, we have participated in the planning for SOLVE implementation through attendance at science team meetings, in planning sessions, and by producing example trajectory-chemistry simulations to examine possible scenarios for Lagrangian flight sampling from the ER-2.

Second, we have made improvements in our modeling capability. For example, the trajectory chemistry model has been upgraded to use measured albedo input from TOMS reflectivity in calculating photolysis rates along the trajectories. The bromine chemistry mechanism has been

updated in both the CTM and trajectory models, rates are upgraded to JPL 1997, and new rates for NO_y partitioning have been tested. CTM runs have been started to evaluate the latest transport winds from the Data Assimilation Office. This assimilation system, which will be used during SOLVE, is significantly different from previous versions. In addition, the CTM computer code has been increasingly optimized for multiple processors resulting in a substantial decrease in run time. This will allow better turn-around time in the field and enables testing a greater range of scenarios in three dimensions.

Third, progress has been made in understanding systematic differences between models and observations. Trajectory-chemistry simulations from the POLARIS measurements have shown how NO_x and HO_x respond to airmass changes as well as updated rate coefficients [Pierson *et al.*, 1999]. Work is also progressing in quantifying the contributions to the ozone budget in the mid latitude lower stratosphere, which lead to a bias in the model ozone column amounts. The result of this analysis indicates that ozone transport via the assimilated winds largely controls the amount of ozone in the lower stratosphere in all seasons. Improvements in Northern Hemisphere ozone simulation are seen with the most recent assimilation product.

Publications

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TOMS SO₂ Studies

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Research Objectives

This task analyses the information on volcanic eruptions that can be derived from TOMS UV Earth radiance data. Quantitative measurements of both sulfur dioxide and ash mass in volcanic clouds are derived using algorithms developed by this group. As a result the first long-term measurements of the global budget of explosive volcanic sulfur dioxide emissions are possible using the database beginning with Nimbus 7 TOMS in 1978. The work includes algorithm development, analysis of new volcanic eruptions, reassessment of older eruptions, validation, transfer of observing capabilities to operational agencies, and development of new satellite flight proposals to improve the volcanic observations.

Summary of Progress and Results

- Ash algorithm development: Ash clouds can be identified qualitatively in TOMS data by discrimination from Rayleigh scattering. Quantitative algorithms were subsequently developed to compute ash optical depth, effective particle size, and density. The sensitivity to different ash parameters was evaluated. Factors which can produce large errors include index of refraction and ash layer height [Krotkov *et al.*, 1997]. Future instruments need to be equipped to measure the plume height. More lab measurements of the index of refraction of typical ash samples are needed to accurately predict ash densities. Ash particles consist of glass shards, bubble walls, and microcrystals. None are spherical so that Mie theory may not apply to the scattering of ash clouds. Consequently non-sphericity effects were evaluated using T-Matrix methods [Krotkov *et al.*, 1999b]. The errors using Mie theory were generally found to be relatively small.
- The algorithm performance was tested with simultaneous observations of an ash cloud by TOMS and IR channels of AVHRR [Krotkov *et al.*, 1999a]. Differences of effective

temperatures between 10 and 12 micron bands are used to estimate the same ash parameters. The two techniques were found to produce consistent results.

- Development of sulfur dioxide retrieval algorithms: The Version 6 TOMS processing algorithm retrieved sulfur dioxide amounts within 30% based on analysis of simulated data using a radiative transfer model [Krueger, *et al.*, 1995]. However, it failed to retrieve credible ozone amounts and, furthermore, it required an empirical correction that had no physical basis. The use of geometric paths rather than a “radiative transfer” path was found to be responsible. When effective paths are used, the sulfur dioxide and ozone amounts are retrieved within 1%. Implementation of this algorithm for TOMS data required iterative use of a radiative transfer model containing the “correct” ozone and sulfur dioxide vertical distributions to compute the effective path. It was found that the model must contain sulfur dioxide layers at the appropriate altitude.
- Analysis of new eruptions: The last of the original TOMS instruments was flown on Meteor 3-5. It collected data from 1991 to December 1994. The launch of its successor, Earth Probe TOMS, was delayed from 1994 to July 1996 because of difficulties with the Pegasus XL launch vehicle. This produced the only gap in coverage of eruptions in the entire TOMS record to date. Fortunately, this period has been quiet with no large eruptions and few small eruptions. The largest, Nyamuragira (Zaire), in December 1996 erupted effusively for about 2 weeks and produced less than 1 Mt of SO₂. Other eruptions that were analyzed included Montserrat, Shishaldin, and Popocatepetl.
- Reanalysis of old eruptions: The ash algorithm permits analysis of a second volcanic cloud component. Reanalysis of the data base using the new ash and SO₂ algorithms has started.
- Validation: Volcanic cloud measurements are notoriously hard to validate because of their great size and transient, infrequent nature. An experiment was sponsored by our group in 1997 to intercompare COSPEC and TOMS data [Schaefer *et al.*, 1997]. Initially, calibration difference between COSPEC instruments were evaluated and corrected by simultaneous measurements of a power plant plume in Arizona. Subsequently, coordinated measurements of passive emissions of sulfur dioxide from Popocatepetl by COSPEC underflights and EP TOMS overflights resulted in a successful comparison. A comparison was possible because EP was flying in a low orbit and TOMS was operated in a special “stare” mode for noise reduction because of the low density of sulfur dioxide compared with explosive eruptions. However, satisfactory agreement within 20% was found.
- Transfer of observing capabilities to operational agencies: TOMS data production software was installed on NOAA operational computers to enable personnel in the Washington VAAC to review the playback data in near realtime. A similar capability was installed for support of the USGS HSS facility. Related software was delivered to the Anchorage NWS facility for collection of EP TOMS data in realtime. This program continued until the primary transmitter on EP failed in late 1997.
- New flight proposals: We proposed the VOLCAM volcanic hazard mission to the Earth System Sciences Pathfinder-2 A/O in 1998 based on UV and IR cameras piggybacked on geostationary satellites to provide 15 minute time resolution data for volcanic research and aviation safety. This proposal was selected as an ESSP alternate mission with an option to proceed independently in a joint NASA - NOAA program. The joint mission will consist of

the VOLCAM UV camera and an ocean color Special Events Imager to be flown on GOES O in 2004, providing funds are available in the NASA budget.

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Modeling and Analysis of the Lower Stratospheric Radiation Field

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Research Objectives

The goals of our research effort for NASA's Upper Atmospheric Research Program (UARP) are to: (1) calculate a set of photolysis rate coefficients or j -values for photochemical reactions of interest in the lower stratosphere and upper troposphere, calculated along the ER-2 flight track for each flight during high altitude ER-2 aircraft campaigns, most notably during the 1997 NASA-sponsored Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) field campaign based in Fairbanks, Alaska; (2) provide a consistency check based on our theoretical modeling for actinic fluxes (and the j -values derived therefrom) obtained by Environment Canada's Composition and Photodissociative Flux Measurement (CPFM) instrument aboard the ER-2; (3) provide a consistency check based on our theoretical modeling for j -values calculated from observed species concentrations, specifically for the photolysis of NO₂ and ClONO₂; and (4) provide an ozone climatology for the ER-2 campaigns, based on a comparison between *in situ* ozonesonde measurements, Total Ozone Mapping Spectrometer (TOMS) total ozone measurements and other ground-based ozone observations.

Summary of Progress and Results

The primary data product of The Johns Hopkins University Applied Physics Laboratory (APL) Theory Team is a set of photolysis rate coefficients or j -values for photochemical reactions of interest in the lower stratosphere and upper troposphere, calculated along the ER-2 flight track for each flight during the POLARIS campaign. These calculated j -values can be compared with those obtained with Environment Canada's Composition and Photodissociative Flux Measurement (CPFM) instrument aboard the ER-2 and with j -values calculated from observed species concentrations. They can also be incorporated into photochemical models used by a variety of instrument groups and other theory groups in their data analysis.

Radiation field calculations are only as good as the inputs to these models. Therefore, a considerable portion of our effort is spent in acquiring and assessing the quality of the input model atmospheres used, with emphasis placed on an accurate description of the total column

ozone and partial column above the ER-2 along the flight tracks. We work cooperatively with other groups to provide additional data products, in particular with NASA Goddard to acquire higher resolution (level 2) TOMS total ozone data than used in prior ER-2 missions, and with the University of Alaska at Fairbanks Geophysical Institute to coordinate their launching of ozone sondes simultaneous with each ER-2 flight. Analysis of these ozone datasets, as well as Environment Canada's Brewer spectroradiometer data, allowed us to establish the seasonal trend of diminishing total ozone over Fairbanks during the POLARIS campaign (a decrease of almost 30 Dobson Units each month), as well as a composite climatology of pressure, temperature and ozone profiles for each deployment. Ozone variability was found to be greatest at altitudes between the tropopause and ER-2 cruise altitude.

Our j -values are calculated using TOMS total ozone data and climatological profiles obtained from the ozonesonde dataset for comparison with the j -values obtained with the CPFM *in situ* spectroradiometer data. While there were significant discrepancies in the j -values produced by our group and those observed by the CPFM instrument and calculated by the JPL theory team during the 1994 ASHOE/MAESA campaign (often 50% differences for $j(\text{NO}_2)$ and factors of 2–3 for $j(\text{O}_3)$), working cooperatively with these groups in the field during POLARIS has significantly reduced these differences in the radiation field to the level of the uncertainties in the cross sections/quantum yields (typically within 5% for $j(\text{NO}_2)$ and better than 25% for $j(\text{O}_3)$). This excellent agreement between the CPFM and two independently-calculated radiation field models provides a validation of the CPFM dataset, which holds the advantage of finer spatial resolution than the TOMS satellite data, as well as simultaneity with the *in situ* trace species observations. We have therefore also calculated a comparable set of j -values which use the CPFM observations of overhead ozone and effective surface albedo as inputs, which agrees well with the calculations of the JPL theory team.

The largest remaining uncertainties in the j -value calculations are our knowledge of the cloud and surface reflectivity beneath the ER-2. The fish-eye camera flown with the CPFM and AVHRR data have proven valuable when trying to distinguish between surfaces of comparable surface reflectivity in the polar region, i.e., ice cover and low-lying clouds

One of the most important scientific questions that can be directly addressed by our radiation field calculations (and validated by the POLARIS dataset) is the sensitivity of certain j -values to input conditions: total ozone, ozone profile, season or solar zenith angle, effective surface albedo, cloud height and atmospheric refraction. The wide range of geography and seasons covered by the POLARIS mission will allow us to assess the relative importance of each of these factors, with an emphasis placed on j -values for the important species O_3 , NO_2 , HNO_3 and ClONO_2 .

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Investigation of the Photochemical Processes that Control Stratospheric Ozone

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Research Objectives

This work focuses on studies of the photochemistry of species that influence ozone abundance in the lower stratosphere. Remote and *in situ* data sets are combined and analyzed with the aid of photochemical model calculations to gain a better understanding of the influence of aerosol-mediated chemistry on the partitioning of inorganic chlorine (Cl_y) and reactive nitrogen (NO_y).

Summary of Results

Based on remote observations from the Atmospheric Trace Molecule Spectroscopy (ATMOS) space shuttle instrument and *in situ* measurements from ER-2 aircraft and balloon instruments, we have developed climatologies for correlations of long-lived trace species, such as CH_4 , N_2O , NO_y , and O_3 [Herman *et al.*, 1998; Michelsen *et al.*, 1998a, b]. We have used these correlations to aid in determining photochemical histories of air masses [Herman *et al.*, 1998; Jost *et al.*, 1998; Michelsen *et al.*, 1998b, 1999a, b; Manney *et al.*, 1999a, b], to intercompare observations from different instruments and platforms [Michelsen *et al.*, 1999a], to identify regions of dynamical isolation and mixing [Herman *et al.*, 1998; Jost *et al.*, 1998; Michelsen *et al.*, 1998a, b, 1999a, b], and to infer one species abundance from measurements of another [Michelsen *et al.*, 1999b].

We have shown that aerosol-mediated reactions proceeding in the lower stratosphere are likely to influence the partitioning of Cl_y and NO_y species at temperatures between 200 and 210 K, even under low to moderate aerosol loading ($<10 \mu\text{m}^2/\text{cm}^3$) [Webster *et al.*, 1998a, b; Michelsen *et al.*, 1999c]. Under low-ozone conditions, as currently found in the Antarctic polar spring, these reactions have little or no effect, even when aerosol abundances are high and temperatures are low [Michelsen *et al.*, 1999b]. Under such conditions, HCl makes up more than 90% of the available Cl_y inside the vortex (compared to 60-70% outside the vortex), and NO_x constitutes 40-60% of NO_y inside the vortex (compared to $\leq 10\%$ outside the vortex) until the vortex breaks. The persistence of this partitioning of Cl_y and NO_y throughout the spring indicates that very little ozone-rich extra-vortex air mixes into the lower Antarctic vortex during austral spring [Michelsen *et al.*, 1999b].

In order to implement current parameterizations based on the most recently measured rates for these heterogeneous reactions, we parameterized the activity of H^+ in aqueous sulfuric acid solutions, which facilitated the inclusion of these rates in the photochemical model [Michelsen *et*

al., 1998c]. We also performed a sensitivity test of the contribution of the long-wavelength, triplet-state photolytic pathway for HOCl to the abundance of OH, which was hypothesized to have an impact on OH for high solar zenith angles; we demonstrated that HOCl photolysis via this electronic state has little effect on OH abundance under most atmospheric conditions [Barnes *et al.*, 1998].

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Evaluating the Information Content of Newly Retrieved SAGEII NO₂ Measurements in the Lower Stratosphere

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Original Research Objectives

- Validate SAGE II NO₂ data using coincident measurements from ATMOS, HALOE, Lauder columns, LIMS, CLAES, ISAMS, ILAS, and balloons accounting for diurnal variations of NO₂ in the SAGE slant column, search for possible remaining aerosol interference in the NO₂ channel, and assess measurement errors, and temperature/pressure conversion errors in the SAGE retrieval.
- Determine if secular changes exist in the stratospheric NO₂ density over the life of SAGE I/II.

Redirected Research Objectives

- Calculate ozone trends in the stratosphere from Dobson Umkehr measurements.
 - Determine the vertical profile of trends at Arosa by using a sophisticated statistical model (MARCH) to separate solar, aerosol, and QBO effects on Dobson Umkehr measurements.
 - Compare Umkehr trends with SBUV and SAGE I/II trends in the stratosphere.

Summary of Progress and Results

Due to delays in the availability of the SAGE II v5.96 NO₂ data, this research was substantially redirected into studying Ozone trends in support of the SPARC/IOC/GAW Ozone Trends Assessment. Therefore, we report here results from that trend assessment as well as from the NO₂ evaluations.

Using temporal/spatial coincidences for SAGE II NO₂ with ATMOS and HALOE NO₂ data to validate SAGE II versions 5.931, 5.96, 6.0a and 6.0b, four ATMOS missions were considered;

SpaceLab-3 (1985), ATLAS-1 (1992), ATLAS-2 (1993) and ATLAS-3 (1994), considering only same event - sunrise/sunrise and sunset/sunset - occultations. Temporal/spatial coincidence criteria used were +/- 24 hrs and a 1500-km ground radius. SAGE II v5.931 exhibited lower NO₂ values as compared to ATMOS, while v5.96 demonstrated an increase from v5.931 resulting in relatively good agreement with ATMOS. Version 6.0 results are considerably larger than ATMOS NO₂ throughout the vertical profile. This bias was found to be due to some unreconciled inversion problems to be addressed in the anticipated v6.0c.

For ATMOS mission profiles not included in the above coincidence criterion, we looked at time series NO₂ contours in altitude and latitude for each ATMOS mission range, and its coincident SAGE II version 5.931, 5.96, (6.0a and 6.0b where available) ranges. Similar HALOE monthly overlapping periods were also employed to validate observed results. Analysis of mission averages corroborated individual coincidence results and a consistency check using HALOE time series resulted in no additional discrepancies. We anticipate analyzing SAGE II version 6.0c data immediately upon its expected release in December 1999.

Dobson Umkehr measurements between 1979 and 1998 were used to assess potential drifts in SAGE and SBUV observations and to estimate annual ozone trends at mid-latitudes. Comparisons of Umkehr time series to SAGE I/II time series constrains the potential drift in SAGE I/II ozone to approximately 0.2 ± 0.2 %/year [WMO, 1998; Newchurch *et al.*, 1998]. The combined trends of Umkehr, SAGE I/II, and SBUV(2) indicate continued significant ozone decline throughout the stratosphere with a maximum of -0.8 ± 0.2 (2σ) %/year at 40 km and a minimum trend of -0.1 ± 0.1 (2σ) %/year at 25 km [Randel *et al.*, 1999; Cunnold *et al.*, 1999; Newchurch *et al.*, 1999].

The trends at Arosa derived from a Multivariate AutoRegressive Combined Harmonics (MARCH) statistical model are systematically more negative, but within the range of 95% uncertainty, compared to the results by the Standard statistical model. The aerosol, solar, and QBO effects on Umkehr ozone at Arosa are separated by the MARCH model providing additional information on the solar and QBO influences on ozone at mid-latitudes [Newchurch *et al.*, 1999b].

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Meteorological Support for Aircraft Missions

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Research Objectives

Obtain standard meteorological data and forecast information for use on NASA sponsored stratospheric aircraft missions.

Summary of Progress and Results

UNIX based workstation has been regularly used in the field on aircraft field missions. This support machine was utilized on the AASE II, SPADE, ASHOE/MAESA, STRAT, POLARIS, and ACCENT field missions. Data assimilation products and personnel from Code 910.3 were utilized to support the POLARIS, STRAT and ASHOE/MAESA missions. Meteorological analyses, radiosondes, ozonesondes, and forecast data were provided as standard products to mission participants. The ASHOE/MAESA mission was completed in 1995, the VOTE/TOTE mission was completed in 1996, and the STRAT mission extended through 1997 as part of POLARIS. We provided full support for the POLARIS experiment, and for balloon flights during 1997 and 1998, and the ACCENT mission. We are currently upgrading our system to a simpler lap-top based system for the 1999-2000 SOLVE mission (leveraging off of AEAP ACCENT funding to de-bug our system). We are also upgrading our data collection to acquire and store the NCEP twice per day AVN forecast runs, which extend our forecasting ability to 10 hPa.

Publications

None

Modeling of Tracers and Meteorological Data

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Research Objectives

The goal of this task is focussed on the modeling of trace gases and analysis of data obtained from stratospheric aircraft missions. A common theme is the use of the meteorological data products and the trajectory model with aircraft data for aircraft data analysis. We have participated in the SPADE, ASHOE/MAESA, STRAT, POLARIS, ACCENT, and SOLVE missions.

Summary of Progress and Results

During December 1996, the GSFC team participated in the last STRAT deployment, and during the summer of 1997 we participated in 3 POLARIS deployments. Our team will be working on the SOLVE campaign during FY2000. The PI served as co-Project scientist for the STRAT campaign, the POLARIS campaign, and SOLVE campaign. As part of our POLARIS work, we developed products for analyzing the motion of air that had undergone continuous solar illumination (solar exposure). This "solar exposure" quantity is related to the higher levels of NO_x observed in the polar region, and was used as a flight planning tool in conjunction with forecast winds provided by the GEOS-STRAT model of the GSFC Data Assimilation Office. For SOLVE, we will be developing equivalent "darkness" and cold temperature exposure RDF plots. In addition, we will be setting up a polar stratospheric forecasting web page for use by the general community. We presented 4 talks at the STRAT/OMS/POLARIS science team meeting, and have been preparing publications as follow-ups to that meeting.

Publications

Gao, R. S., D. W. Fahey, L. A. Del Negro, S. G. Donnelly, E. R. Keim, J. A. Neuman, E. Teverovskaya, P. O. Wennberg, T. F. Hanisco, E. J. Lanzendorf, M. H. Proffitt, J. J. Margitan, J. C. Wilson, J. W. Elkins, R. M. Stimpfle, R. C. Cohen, C. T. McElroy, T. P. Bui, R. J. Salawitch, S. S. Brown, A. R. Ravishankara, R. W. Portmann, M. K. W. Ko, D. K. Weisenstein, and P. A. Newman, A comparison of observations and model simulations of NO_x/NO_y in the lower stratosphere, *Geophys. Res. Lett.*, 26, 1153-1156, 1999.

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Weinheimer, A. J., D. D. Montzka, T. L. Campos, J. G. Walega, B. A. Ridley, S. G. Donnelly, E. R. Keim, L. A. Del Negro, M. H. Proffitt, J. J. Margitan, K. A. Boering, A. E. Andrews, B. C. Daube, S. C. Wofsy, B. E. Anderson, J. E. Collins, G. W. Sachse, S. A. Vay, J. W. Elkins, P. R. Wamsley, E. L. Atlas, F. Flocke, S. Schauffler, C. W. Webster, R. D. May, M. Loewenstein, J. R. Podolske, T. P. Bui, K. R. Chan, S. W. Bowen, M. R. Schoeberl, L. R. Lait, and P. A. Newman, Comparison of DC-8 and ER-2 species measurements on 8 February 1996: NO, NO_y, O₃, CO₂, CH₄, and N₂O, *J. Geophys. Res.*, 103, 22087-22096, 1998.

Analysis of Far Infrared Experiment Data

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Research Objectives

The three-year research (starting from September 1999) will focus on data analysis to obtain vertical profiles of OH, HO₂, H₂O₂, and HOCl in the stratosphere, and water vapor continuum cross section in the far infrared region using data from three balloon-borne Far-Infra Red Experiments (FIREX) in 1992, 1993, and 1994. These gases play important roles in the stratospheric ozone chemistry.

Summary of Progress and Results

Previously, these FIREX data have been analyzed and resulted in the following five publications: i.e., (a) The analysis results of the 1992 flight data (i.e., O₃, H₂O, HCl, and HF) were successfully used for validation of the satellite-borne Halogen Occultation Experiment (HALOE) measurements of respective species [Russell *et al.*, 1996a, b]; (b) Two papers were published on HBr in the stratosphere from the 1993 and 1994 flight data [Carlotti *et al.*, 1995, and Nolt *et al.*, 1997] for better understanding of bromine chemistry; and (c) From the 1994 data, accurate frequency measurement of O₃ and H₂O was made [Natale *et al.*, 1997] which is important for spectral data analysis.

It is planned to resume data analysis for the following expected results:

- Simultaneous profiles of OH, HO₂, H₂O₂, and HOCl and H₂O from the 1992 and 1994 data;
- Diurnal variations of OH, HO₂, H₂O₂, and HOCl from the 1992 and 1994 data; and
- The continuum emission by H₂O as a function of pressure and temperature from the 1992 and 1994 data. This water vapor continuum information for various pressures of the atmosphere will be obtained first time from real atmospheric measurement.

Publications

Carlotti, M. P., P. A. R. Ade, B. Carli, P. Ciapallini, U. Cortesi, M. J. Griffin, G. Leppri, F. Mencaraglia, A. G. Muray, I. G. Nolt, J. H. Park, and J. V. Rodostitz, Measurement of stratospheric HBr using high resolution far infrared spectroscopy, *Geophys. Res. Lett.*, 22, 3207-3210, 1995.

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Meteorological Support for Airborne Missions

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Research Objectives

The objectives of this task are twofold. First, we provide meteorological guidance on tropospheric weather to the airborne missions for NASA's Upper Atmosphere Research Program. This includes providing, in real time, and archiving, extensive meteorological satellite datasets for use by the mission scientist and by the science team. Second, there are three areas of scientific analysis for which we are using data from UARP airborne field missions: water vapor and subvisible cirrus clouds in the upper tropical troposphere, water vapor in the upper winter arctic troposphere and lower stratosphere, and inertia-gravity waves. The first of these issues is fundamental to the input of water vapor into the stratosphere, which is an important factor in stratospheric gas phase chemistry and for the formation of Polar Stratospheric Clouds (PSCs). The chemistry on PSCs, in turn, is responsible for much of the ozone loss to chlorinated hydrocarbons. The second area, water vapor in the arctic upper troposphere and lower stratosphere, is potentially important to the formation of ice clouds that can have similar chemical effects as the PSCs. Finally, inertia-gravity waves are important both because they produce turbulence, which can effect vertical mixing of stratospheric trace constituents, and because they produce temperature deviations that can produce subvisible cirrus clouds.

Summary of Progress and Results

During Fiscal Year 1997, our group provided meteorological, satellite, and computer support for the last field component of STRAT, during December 1996. Similar support was provided for the entire field phase of POLARIS, during the spring, summer, and fall deployments in FY97. We provided animated satellite image loops on a real-time basis using our in-house developed archival and processing system. These were of particular interest for ascertaining the locations of the dips in the ER-2 north and south survey flights. They were critical for the stacked flights, involving half-hour legs at altitudes as low as 42000 feet (12.5 km). The most crucial piece of information is the altitude of the cloud tops, since the aircraft instruments can be compromised by extensive time within clouds. We also provided the necessary field computers for the project scientist, numerical prediction, and our own meteorology group.

We have archived the meteorological satellite data, and provided selected products to the science team, including: (1) along-the-flight-track exchange files of reflectivity, cloud height, and underlying satellite IR brightness temperature, and (2) postscript files of satellite imagery with overlaid meteorological fields and flight tracks.

To deal with the three areas of scientific analysis, we have developed some important analysis tools. The most notable of these is the so-called "convective influence" calculation, whereby we calculate, using a combination of back trajectories and meteorological satellite data, the amount and age of recent "convective influence" on an air parcel. This, in conjunction with lightning flash rate data, has been very useful in interpreting tropospheric NO for another research task separate from this one. For this task, we used it to evaluate whether subvisible cirrus clouds observed during the 1995-1996 Tropical Ozone Transport Experiment/Vortex Ozone Transport Experiment (TOTE/VOTE) were produced by local cooling and ice nucleation or were a long-lived outflow from convection. We found good correspondence between the locations of different types of near-tropopause cirrus and the origins of the air, with smooth laminar cirrus clearly the result of local cooling, and lumpier clouds the apparent outflow of convection. Notably, it appears that some of this convective outflow can last several days, based on our calculations. We also noted the presence of inertia-gravity waves and their characteristics. These waves have a very good correspondence to the sloping cloud shapes, indicating that the cooling associated with these waves is probably responsible for the clouds.

This last result is significant, since it lends support to a hypothesis that is the result of modeling work. This hypothesis suggests that long-period waves produce cirrus clouds, which are then heated and lofted into the stratosphere. As the clouds grow, large particles fall out, dehydrating the air. In effect, this mechanism will move air into the stratosphere and dehydrate it at the same time, possibly resolving a crucial question of how very dry air gets into the lower tropical stratosphere.

Publications

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Tracer Evolution at High Latitudes in Winter (SOLVE)

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Research Objectives

This project is an investigation of tracer budgets in the Arctic vortex in wintertime, using a three-dimensional chemical transport model and data from the forthcoming SOLVE experiment.

Summary of Progress and Results

Work at this stage has comprised preparation for the forthcoming SOLVE mission. The main effort is the application of a three-dimensional chemical transport model based on an isentropic coordinate (which is being developed under other funding) to the stratosphere, using winds from the NASA/DAO assimilation model. This model will be run operationally during the SOLVE ER-2 deployments, and will be used in the analysis of tracer measurements.

Publications

None

Impact of Descending Polar Mesospheric NO_x on Stratospheric Ozone

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Research Objectives

The goal of this program is to use data from the Polar Ozone and Aerosol Measurement (POAM) II and III instruments to investigate the effects of descending polar mesospheric NO_x on stratospheric ozone. The work includes analysis of POAM II NO₂ and ozone data in both the Northern and Southern Hemispheres from 1994 to 1996, and of POAM III data as they become available. Our first objective is to quantify the enhancements in stratospheric NO₂, if any, from wintertime production of NO_x in the mesosphere and thermosphere. We are also analyzing NO₂ data from the Halogen Occultation Experiment (HALOE) to extend the time series of possible enhancements back to 1991. Ozone data from POAM, HALOE and the Stratosphere Aerosol and Gas Experiment (SAGE) and the Microwave Limb Sounder (MLS) are used to quantify effects of any enhanced NO_x on stratospheric ozone. A photochemical box model, run along trajectories appropriate to the POAM measurements, will be used to investigate the detailed longitudinal variations in NO₂ and ozone in both hemispheres. Two-dimensional model calculations will be used to investigate the interannual variation in the amount of NO_x transported to the stratosphere, and the resulting effects on ozone.

Summary of Progress and Results

The POAM II data were analyzed and clearly showed the effects of mesospheric NO_x descending to the stratosphere during the Southern Hemisphere winter of 1994. Smaller effects were noticeable in the winter of 1995, and the enhancements appeared negligible in 1996. Correlated with the stratospheric NO_x enhancements were localized reductions in ozone of up to about 40%. POAM III data from the first year of operations were also analyzed, and showed effects similar to those in 1995. All of these enhancements were correlated with the geomagnetic Ap index, suggesting that the interannual variability in stratospheric NO_x enhancements in the Southern Hemisphere is controlled by the source region. HALOE NO_x showed similar variations at high southern latitudes during 1994 to 1996. We have also contributed to the analysis of HALOE NO_x measurements back to 1991; in agreement with the conclusions drawn from the POAM measurements, stratospheric NO_x enhancements seem to be correlated with the Ap index. The magnitude of the global effect depends not only on the source region, but also on the size of the vortex in which the originally formed NO is contained. We found that when spread over most of

the Southern Hemisphere, the maximum excess NO_x represented a few percent increase over the baseline.

When analyzed in the same manner as the Southern Hemisphere data, Northern Hemisphere measurements from POAM II during the winters of 1993-1994, 1994-1995, and 1995-1996 showed little evidence for stratospheric NO_x enhancements. However, NO_x enhancements in the northern hemisphere are more difficult to quantify. The complexities arise because of the increased dynamical activity in the north, leading to an unstable and asymmetric polar vortex. It is thus possible that the same method of analysis cannot be applied to both the Northern and Southern Hemispheres. Indeed, there is a possibility that NO_x might descend to the upper stratosphere in the Northern Hemisphere vortex, and then be pulled out to lower latitudes via vortex filaments; this would preclude observation by POAM. This possibility is currently being investigated using HALOE data.

Publications

Randall, C. E., D. W. Rusch, R. M. Bevilacqua, K. W. Hoppel, and J. D. Lumpe, Polar Ozone and Aerosol Measurement (POAM) II stratospheric NO₂, 1993-1996, *J. Geophys. Res.*, 103, 28361-28371, 1998.

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Reprocessing of the Nimbus 7 LIMS Data Set

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Research Objectives

This effort is aimed at generating an improved version of the 1978/1979 Nimbus 7 LIMS dataset that is compatible with those from UARS. The HITRAN 92/96 line parameters are to be used for the reprocessing.

Summary of Progress and Results

The operational reprocessing of the 216 days of LIMS Level 2 (profile) data is underway and will be complete by early 2000. Improvements have been found for all LIMS parameters, due to updates in spectroscopy since 1980 and in other aspects of the forward model. We have also realized an important improvement in our knowledge of the spacecraft attitude, based on a matching of the calculated and LIMS-observed CO₂ radiances in the lower mesosphere for each scan during a first pass of the algorithm to retrieve temperature versus pressure T(p) profiles. This update to the attitude information was then used for the final retrieval of T(p) and then for the species profiles. The minor seasonal and hemispheric asymmetries in the original, archived (V5) LIMS data have been largely corrected with this update. Vertical resolution of the products has been improved, and profile spacing along an orbit is 1.6 degrees of latitude or less (at higher latitudes). First-order aerosol corrections have also been applied to all the species. As a result of these changes, the revised data are much more compatible with those from UARS. Further, this revised data set can be considered as a precursor to that expected from the HIRDLS experiment on EOS CHEM.

Brief summaries of the improvements are given here. The revised temperatures are warmer in the mesosphere, but colder at the tropical tropopause—both in excellent agreement with correlative measurements for the middle atmosphere. Day/night differences indicate tidal

signatures. Revised ozone is slightly larger in the upper stratosphere, but significantly lower in the lower stratosphere. These changes generally agree with other measurements of ozone within their combined error bars. Day minus night ozone is of order +5% or less in the middle stratosphere. Non-LTE effects in daytime ozone in the mesosphere are smaller, but still present. The nitric acid distributions are nearly unchanged except in the upper stratosphere, where the interfering effects of CO₂ are known better and are being accounted for in the retrieval. Water vapor has better hemispheric and seasonal symmetry and ranges from about 3.5 ppmv in the lower tropical stratosphere to about 6.5 ppmv in the upper stratosphere and at higher latitudes. The nighttime NO₂ is nearly 20% less than V5 in the upper stratosphere and in good agreement with the HALOE sunset values of NO plus NO₂. Daytime NO₂ is decreased by a smaller percentage. In addition, the revised Level 2 product contains profiles of geopotential height that have been referenced to the 50-mb heights that were originally provided to the Nimbus 7 Teams by the National Meteorological Center (NMC).

The revised Level 2 profiles are being screened for obvious cirrus and polar stratospheric cloud signature effects in the ozone profiles. Then they are written onto CD-ROM media in ASCII format for easy use and eventual archival at the Goddard DAAC.

Because of the current interest in the character and seasonal variation in the subtropical barrier of the lower stratosphere, Remsberg and Bhatt [1996] used the seasonal progression of the daily zonal variance of LIMS V5 nitric acid as an indicator of wave activity and the expansion and contraction of the so-called "surf zone" and its latitudinal boundaries. Nitric acid is a good tracer at low latitudes, because its equilibrium values have a meridional gradient that varies with the seasonal solar zenith angle. It is also unaffected by bias errors that degrade the calculation of absolute vorticity at low latitudes. Remsberg and Bhatt found that a region of tight latitudinal gradients developed and was shifted from about 25°N latitude to near the Equator in late fall to mid winter. Its position retreated by late spring. This finding is clear evidence that the so-called "tropical pipe" is not fixed in width or latitude throughout the year. This result is specific to the easterly phase of the QBO; its character should be somewhat different for the westerly phase.

Publications

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Analysis of Atmospheric Trace Molecule Spectroscopy (ATMOS) Spectra for Trace Gases

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Research Objectives

The main objective of this research is the analysis of ATMOS solar spectra recorded during its 4 shuttle missions to obtain improved profile measurements of important atmospheric gases. Emphasis is on studies of molecules involved in O₃ chemistry in the upper troposphere and lower stratosphere. Secondary objectives include refinements to algorithms for retrievals of trace gases from the ATMOS solar occultation spectra, analyses of the ATMOS observations for aerosol and cloud extinction, and studies of atmospheric chemistry based on the ATMOS version 3.1 profiles. As required, studies are conducted to improve spectroscopic parameters for ATMOS inversions, provide updates to the public spectroscopic databases, and validate the ATMOS profiles.

Summary of Progress and Results

Vertical profiles of infrared cirrus extinction have been derived from tropical and subtropical upper tropospheric ATMOS spectra recorded during the November 1994 ATLAS 3 mission. The presence of large numbers of small ice crystals is inferred from the appearance of broad extinction features in the 8-12 μm window. These features were observed near the tropopause and at lower altitudes. Vertical profiles of ice extinction (km^{-1}) in microwindows have been retrieved from the spectra and analyzed with a model for randomly oriented spheroidal ice crystals. An area-equivalent radius of 6 μm is estimated for the smallest ice crystals observed. Direct penetration of clouds into the lower stratosphere is inferred from cloud extinction extending to 20 km.

Vertical mixing ratio profiles of HCN, C₂H₂, CO, and C₂H₆ were also retrieved from the ATLAS 3 tropical and subtropical spectra. Elevated mixing ratios were measured for these 4 molecules during several of the occultations. The positive correlations obtained between simultaneously measured mixing ratios suggest that the enhancements were likely the result of surface emissions, most likely biomass burning and/or urban industrial pollution, followed by common injection by deep convective transport of the gases to the upper troposphere. The elevated HCN may account for at least part of the "missing NO_y" in the upper troposphere. Recent ground-based observations from Mauna Loa suggest the elevated HCN is likely the result of biomass burning.

Observations inside the November 1994 Antarctic stratospheric vortex and inside the April 1993 remnant vortex show elevated mixing ratios of CO near 700 K (~27 km). The observations indicate the descent of mesospheric air to the mid-stratosphere in both hemispheres. The elevated CO occurs near the location of a pocket of elevated NO_y observed in the Antarctic. No enhancement in NO_y is indicated by the Arctic vortex observations.

Partial columns of N₂O, CH₄, O₃, and HNO₃ have been retrieved from Kitt Peak spectra for 2 layers, 14-20 and 20-50 km. Measurements of N₂O versus CH₄ for the 14-20 km layer show a compact positive correlation. No evidence was found for a variation in the mean relation with season. The 20-50 km of N₂O versus CH₄ 20-50 km columns also show a compact relation despite the shorter lifetimes of both molecules. Compact O₃ vs. HNO₃ relations are also measured provided observations recorded shortly after the Mt. Pinatubo volcanic eruption are excluded. The N₂O-CH₄ and O₃-HNO₃ columns correlations have been compared with corresponding relations calculated from ATMOS profile measurements recorded near the same latitude in November 1994, taking into account the more limited vertical resolution of the Kitt Peak measurements.

A paper describing the HITRAN 1996 database was written for a special issue of the *Journal of Quantitative Spectroscopy and Radiative Transfer*. Articles were also written documenting the HITRAN updates for O₃, NO, HNO₃, ClONO₂, HBr, HI, NO₂ and SO₂. As documented in the partial list below, additional papers were published reporting stratospheric, tropospheric, and spectroscopic studies in support of this NASA task.

Publications (Partial List)

Coffey, M. T., A. Goldman, J. W. Hannigan, W. G. Mankin, W. G. Schoenfeld, C. P. Rinsland, C. Bernardo, and D. W. T. Griffith, Improved vibration-rotation (0-1) HBr line parameters for validating high resolution infrared atmospheric measurements, *J. Quant. Spectrosc. Radiat. Trans.*, 60, 863-867, 1998.

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**U. S. Algorithm Development for the Canadian Atmospheric Chemistry Experiment (ACE)
SCISAT-1 Mission**

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Research Objectives

The objective of this task is to provide updates to the existing Stratospheric Aerosol and Gas Experiment (SAGE) and Atmospheric Trace Molecule Spectroscopy (ATMOS) retrieval algorithms, create a spectroscopic database for ACE, and provide instrument engineering consultation to the ACE principal investigator and to ABB Bomem Inc., the prime instrument provider for ACE.

Summary of Progress and Results

Contracts are now in place to support the first year of United States support of ACE. Regular telecons have been held between ACE team co-investigators in the United States and Canada and several reviews and meetings have been attended in Canada in support of ACE development. Marty McHugh (G&A Technical Software, Newport News, Virginia) has been hired to support ACE based on his software development experience for the Halogen Occultation Experiment (HALOE). He is consulting on software including procedures for implementing diurnal corrections to NO and NO₂ profiles. Initial discussions have resulted in a procedure for using the ACE visible arrays and/or an accurate shaft encoder for precise pointing angle determination. The improved pointing knowledge should result in more accurate retrievals of pressure and temperature profiles. Dr. Mark Abrams (Abrams and Associates, Fort Wayne, Indiana) has provided ATMOS (version 2) heritage algorithms to the ACE team at the University of Waterloo for pressure-temperature and molecular constituent sounding and a database of ATMOS measurements from its 4 shuttle missions. Dr. Abrams is tasked with supporting the implementation, demonstration, and validation of the ATMOS codes for the ACE mission. These activities will include successful installation and testing of ATMOS codes and scripts on the ACE computer systems. Dr. Abrams will present quarterly instructional sessions for the ACE team at the University of Waterloo, Canada. Dr. Abrams is also tasked with obtaining an

export license (DSP-5) and Technical Assistance Agreement (DSP-83) consistent with current United States Government International Traffic in Arms Regulations (ITARS). Telecons have resulted in a revised ACE Fourier transform spectrometer (FTS) design. The revised design is fully tilt and sheer compensated based on suggestions by Dr. Donald E. Jennings of NASA Goddard.

Publications

None

Model Interpretation of Aircraft, Balloon, and Shuttle Data

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Research Objectives

Our program of research was designed to investigate factors that regulate the composition of the stratosphere and upper troposphere. Our work was motivated by the need to gain an improved understanding of the effects of anthropogenic activity on the abundance of ozone and the oxidizing capacity of the upper troposphere. We proposed to analyze a variety of *in situ* and remote measurements using existing photochemical, dynamical, and thermodynamic models to better quantify processes that currently limit our ability to accurately predict past and future changes in composition due to variations in trace gases, aerosol loading, and temperature driven by human activity. Our proposed analyses focused on the following tasks:

- (1) Understanding the processes that regulate the abundance of the hydroxyl radical (OH) in the upper troposphere.
- (2) Better quantification of the processes that regulate the abundance of the chlorine, nitrogen, and hydrogen radicals that react with ozone to improve our understanding of the role of chemistry in driving the observed long-term reduction of stratospheric ozone.
- (3) Examination of tracers of long-lived atmospheric motion to define rates of exchange of air between the tropical and mid-latitude lower and middle stratosphere.
- (4) Analysis of satellite data for ozone, temperature, chlorine monoxide, and gas phase nitric acid (HNO_3) to better quantify the relative role of chemistry versus dynamics in the seasonal change in ozone during the period of rapid ozone loss in the Antarctic and Arctic winter stratosphere and to define the phase and composition of polar stratospheric clouds during this time period.

Summary of Progress and Results

We have co-authored many published papers during the period of support. The major findings are briefly summarized in categories related to the proposed research tasks given above:

- (1) The upper troposphere is considerably more photochemically active than previously thought, as indicated by measured concentrations of OH that are factors of 3 to 4 higher than calculated values based solely on production of OH from oxidation of H_2O and CH_4 .

Production of OH from photolysis of acetone and hydrogen peroxide is a possible explanation for the observations [Wennberg *et al.*, 1998]. Adding photolysis of acetone to a model improves the agreement between measured and modeled NO_x/NO_y in the upper troposphere due to the important role of peroxy acetyl nitrate [Keim *et al.*, 1999].

- (2) At 40 km, the loss rate of ozone computed from balloon-borne measurements of chlorine, nitrogen, and hydrogen radicals agrees well with theory and with the computed production rate of ozone. At higher altitudes (e.g., 45 to 60 km), production of ozone exceeds loss, but the magnitude of the "ozone deficit" is sensitive to small errors in the concentration of O₃ [Osterman *et al.*, 1997]; there is a relatively good understanding of the dependence of NO_x/NO_y on aerosol surface area, despite discrepancies in detailed aspects of the partitioning of nitrogen oxide gases [Kondo *et al.*, 1997; Sen *et al.*, 1998]; revisions to the JPL97-4 chemistry, most likely the OH + NO₂ + M reaction, are required to accurately describe the measured NO_x/NO_y ratio observed during POLARIS [Osterman *et al.*, 1999; Gao *et al.*, 1999]; the abundance of OH observed by the FIRS-2 balloon borne instrument agrees well with photochemical theory to altitudes as high as 50 km, in contrast to shuttle-borne observations obtained by the MAHRSI instrument, but the [OH]/[HO₂] ratio suggests either a missing process converting OH to HO₂ or else improper treatment of the ratio of the rates of the OH + O and HO₂ + O reactions [Jucks *et al.*, 1998]; our understanding of the budget and partitioning of Cl species is complete and accurate during conditions of low aerosol loading and warm temperature that prevailed during POLARIS [Sen *et al.*, *JGR*, 1999]; iodine chemistry can not be responsible for the trends in lower stratospheric ozone observed during the past several decades, based on analysis of high resolution, high airmass solar spectra near 445 nm wavelength obtained at Fritz Peak, CO [Wennberg *et al.*, 1997].
- (3) The previously identified isolation of mid-latitude and tropical air near 20 km extends to higher altitudes, with an exchange time of approximately 16 months, based on an analyses of OMS data [Herman *et al.*, 1998]; the entrainment time scale of mid-latitude air into the tropical upwelling region during 1996 and 1997 is considerably less found by a similar study that focused on observations obtained during 1994, for reasons that are not understood [Flocke *et al.*, 1999].
- (4) PSCs are most likely composed of ternary solutions during their incipient phase of formation, and nitric acid dihydrate appears to be the first solid phase to form, based on analysis of MLS observations of HNO₃ [Santee *et al.*, 1998]; ATMOS and ER-2 observations of NO_y and H₂O + 2 x CH₄ vs N₂O provide evidence for significant levels of denitrification in the Arctic vortex during the winter of 1992/93, in the absence of significant dehydration [Rinsland *et al.*, 1999]; tracer-tracer relationships can be used to diagnose quantitatively the degree of descent and mixing with the polar vortex and the use of CH₄-N₂O-NO_y relationships provides a more accurate framework for estimating the degree of denitrification than the traditional approach of using only the NO_y-N₂O relationship [Rex *et al.*, 1999]. An analysis of a 30 year record revealed a strong correlation between the mean column abundance of O₃ poleward of 63°N during March and the minimum temperature inside the arctic vortex during early March [Salawitch *et al.*, 1998].

Finally, R. Salawitch was co-lead author of the "Upper Stratospheric Processes" chapter of the 1998 WMO O₃ Assessment Report that summarizes recent progress in this area of research.

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Photochemical Modeling of Field Data

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Research Objectives

Analysis of measurements of radicals, reservoir gases, long-lived tracers of atmospheric transport, and aerosol surface area obtained from the ER-2 during POLARIS and previous ER-2 campaigns and the OMS balloon payload to examine our understanding of the photochemical and dynamical processes that regulate O₃ in the lower stratosphere and upper troposphere.

Summary of Progress and Results

We have co-authored numerous published papers during the period of support. The major findings are:

- Generally good agreement between theory and observation of the NO₂/NO ratio over a wide range of latitudes during ASHOE/MAESA and POLARIS, although the NO₂/NO ratio observed in the Concorde exhaust plume was surprisingly less than expected; the rate of the NO + O₃ reaction constitutes the largest source of uncertainty to this system [Gao *et al.*, 1997; Sen *et al.*, 1998; Del Negro *et al.*, 1999].
- Theory and observation of NO_x/NO_y are in much better agreement using recently measured rates for OH + NO₂ + M and OH + HNO₃ than the recommended values given in the JPL97-4 compendium [Sen *et al.*, 1998; Gao *et al.*, 1999; Osterman *et al.*, 1999].
- Evidence for a missing source of HO_x involving photolysis of a reservoir at long-wavelengths ($\lambda > 650$ nm); we speculate that the reservoir is HNO₄ [Wennberg *et al.*, 1999].
- The abundance of stratospheric bromine is about 20% less than previously believed and significant discrepancies exist concerning the organic bromine budget and *in situ* observations of BrO [Wamsley *et al.*, 1998].
- The use of a multi-variate tracer-tracer analysis based on data from the ER-2, balloon, and satellite platforms allows descent, mixing, and the degree of denitrification to be diagnosed inside the Arctic vortex in a more precise manner than previous estimates [Rex *et al.*, 1999].
- Our understanding of the budget and partitioning of Cl species is complete and accurate during conditions of low aerosol loading and warm temperature that prevailed during POLARIS [Sen *et al.*, 1999].

- FIRS-2, MkIV, and ATMOS observations of HCl/Cl_y and surface area do not support the large reductions in HCl/Cl_y due to enhanced aerosol loading that has been seen in the ER-2 data set [Bonne *et al.*, 1999].
- The previously identified isolation of mid-latitude and tropical air near 20 km extends to higher altitudes, with an exchange time of approximately 16 months, based on analyses of OMS data [Herman *et al.*, 1998]; the entrainment time scale of mid-latitude air into the tropical upwelling region during 1996 and 1997 is considerably less found by a similar study that focused on observations obtained during 1994, for reasons that are not understood [Flocke *et al.*, 1999].
- Filaments of air in the tropical stratosphere that have a clear mid-latitude origin are identified and the ages of these parcels are calculated [Jost *et al.*, 1998].
- The upper troposphere is considerably more photochemically active than previously thought; measured concentrations of OH and HO₂ are factors of 3 to 4 higher than calculated based solely on production of HO_x from oxidation of H₂O and CH₄ [Wennberg *et al.*, 1998].

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Predominantly Stratospheric Chemistry

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Analyses of MkIV DC-8 Aircraft Observations

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Research Objectives

The research conducted under this RTOP is to re-analyze the infrared solar absorption spectra measured by the JPL MkIV interferometer during the AAOE and AASE DC-8 missions that took place in 1987, 1989, and 1992. These spectra provide a unique inventory of the stratospheric composition at a time of relatively low chlorine loading and under conditions of both high and low volcanic aerosols. The re-analyzed results have three major advantages over the previously reported and archived column abundance values: (1) The aircraft spectra were ratioed by a MkIV balloon high-sun spectrum in order to eliminate solar and instrumental features. This allowed us to analyze spectral regions which were previously unusable due to the presence of solar features (e.g., CO) or difficult to distinguish from minima in the instrumental continuum spectrum (e.g., CFC-11, CFC-113). (2) Substantial improvements have been made in the mid-infrared spectroscopic linelist since 1992 for molecules such as H₂O, O₃, N₂O, NO₂, HNO₃, etc. Additionally, pseudo-linellists have been developed for some of the heavier molecules (e.g., CFC-11, CF₄, SF₆, CFC-113) which provide a convenient and accurate means of extrapolating the cross-sections to atmospheric pressures and temperatures. (3) Improvements in the spectral fitting software (e.g., multi-gas, wide spectral windows, isotopes) allow a larger fraction of MkIV spectral domain to be analyzed and fitted with much better fidelity. The net result of these three improvements is to greatly improve the accuracy and precision of the retrieved atmospheric gas abundances and to extend the suite of gases measured. The re-analysed DC-8 results are directly comparable with MkIV balloon results, and the ATMOS version 3 results, both of which use the same analysis software as the proposed work here.

Summary of Progress and Results

An inherent feature of the solar absorption technique is that the solar spectrum contains absorption and emission features arising from gases in the solar photosphere. It complicates analysis of atmospheric absorption features of interest if they are blended with solar absorption lines. A successful approach is to ratio the atmospheric limb spectra by a solar spectrum measured high above the Earth's atmosphere, as infrared solar spectrum is highly invariant with respect to time. The resulting atmospheric transmittance spectra are free from solar (and

instrumental) artifacts. Such a removal of solar and instrumental features from the MkIV DC-8 spectra obtained in 1987, 1989, and 1992 was accomplished by ratioing against high-sun balloon spectra, also measured by MkIV in 1989 and 1992 from 38 km altitude. Thirty-one regions between 816 and 4682 cm^{-1} containing discrete solar features were identified and the frequency shift calculated between these absorptions in the high-sun balloon and the DC-8 spectra. The frequency re-sampled high-sun balloon spectra were then degraded to the same spectral resolution as the DC-8 observations and used to ratio the airborne measurements. These fully calibrated DC-8 spectra could then be used to analyze both wide featureless absorption (e.g., CFC-11, CFC-113, CCl_4 , stratospheric sulfate aerosol continuum) and atmospheric absorption previously blended with solar lines (e.g., CO, NO).

The ratioed DC-8 spectra were then analyzed using the latest version of the GFIT spectral fitting algorithm (which is also used for analysis of MkIV balloon spectra and ATMOS version 3 shuttle spectra), and using the latest version of the ATMOS linelist together with the pseudo-linellists. Over 300 spectra, each covering the 650-5650 cm^{-1} region, have been analyzed for 27 different species and their isotopes using the multi-gas, multi-level spectral fitting software. The May and July, 1997, balloon-borne measurements of the atmospheric abundances of ClNO_3 , CF_4 , CFC-12, CFC-11, CCl_4 , HCFC-22, SF_6 , and CFC-113 by the MkIV interferometer above Fairbanks, Alaska, provided an opportunity to comprehensively validate the pseudo-linelist and the analysis software using *in situ* observations of the same gases on board the NASA ER-2. Furthermore, a detailed analysis using the JPL photochemical model constrained by the full suite of remotely observed chlorine- and nitrogen-precursors, reservoirs, and tracers show excellent agreement between calculated and measured radicals that affect loss of stratospheric ozone including ClNO_3 and N_2O_5 , confirming the accuracy of the pseudo-linelist.

Another activity under this task has been the calculation of pseudo-lines to represent broad featureless absorption in the mid-infrared. Pseudo-lines for a number of chlorine-, fluorine-, and nitrogen-bearing compounds (e.g., CFC-12, CFC-11, N_2O_5) have been calculated with exaggerated Doppler widths but with realistic pressure-broadened half-widths (PBHW) to retrieve atmospheric abundances of the gases. The spectroscopic linelist was derived by fitting all of the relevant laboratory spectra simultaneously while solving for the 296 K strength (S) and the Ground State Energy (E'') of each pseudo-line. The PBHW and its temperature dependence were determined "manually". These pseudo-lines have the advantage that they: (1) are in the HITRAN format, and can be conveniently accessed by spectral fitting software in exactly the same manner as all the regular gases. (2) By fitting a physically-based function to the laboratory spectra the consistency of the various laboratory measurements have been assessed. Laboratory spectra which are inconsistent with the others (i.e., negative values of S and E''), have been identified and rejected. (3) The effect of instrumental line shape of the laboratory spectrometer on the measured absorption cross-sections have been removed in calculating the pseudo-lines. This is particularly important when the atmospheric spectra are measured at a better resolution than the laboratory spectra. (4) Several different laboratory data-sets, even with widely different measurement conditions and spectral resolutions, have assimilated into a single pseudo-linelist. Both the ratioed DC-8 spectra and the pseudo-linellists are available on request.

Publications

None

Reanalysis of Nimbus 4 BUV Data

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Research Objectives

The Nimbus 4 BUV (Backscatter UltraViolet) instrument began making measurements of the total column amount of ozone in April of 1970. It operated on a nearly global basis for the first two years in orbit. The instrument continued to operate on a more limited schedule into 1977. These data provide an excellent opportunity to extend the global ozone data record backwards by nearly a decade. The data provide a problem because the calibration is uncertain and the data do not overlap with later satellites.

Summary of Progress and Results

We began this study by focussing on the Antarctic spring. The question was whether we could find any evidence to indicate the presence of the Antarctic ozone hole phenomenon in the early 1970s. Maps of the October mean ozone for 1970 through 1972 indicated a picture much like that for 1979. There was a circumpolar maximum in ozone surrounding a shallow minimum with about 300 DU of ozone. This was consistent with the picture which had been deduced from the sparse station data. Thus the satellite data confirmed that the Antarctic springtime ozone throughout the 1970s was very different from what it has been since the early 1980s.

The conclusions concerning Antarctic ozone were not dependent on a very accurate calibration (within a few percent was sufficient). We next turned to the question of northern mid-latitude and global trends. Here we were asking a question which was much more dependent on the quality of the calibration of the BUV instrument with respect to the later Total Ozone Mapping Spectrometer (TOMS) measurements. Various attempts at establishing an accurate calibration through internal checks have been attempted under other funding. None of these has provided the magic solution.

We have turned to using the imperfect means of calibration by comparison with the ground-based Dobson network. The BUV data in the early 1970s are not as good as those from later satellites. The Dobson data for that period are not as plentiful nor as good as the data for later time periods. Nonetheless, they provide a guide to getting the best relative calibration that we can now make.

We did a standard trend analysis of the zonal mean data from 1978 through 1994. This analysis included terms for mean, seasonal variation, solar cycle, quasi-biennial oscillation (QBO), and noise terms. We then extended this time series backwards using the values of the coefficients for each of the terms. We extended the trend backwards with three different assumptions: (1) linear all the way back to 1970; (2) linear back to 1975 and constant to 1970; and (3) linear to 1978 and constant to 1970. The results of all three of these cases were similar.

At southern mid-latitudes and the equator, the BUV data in the early 1970s fit approximately on the extrapolated trend line after the solar cycle, QBO and other terms were removed. At northern mid-latitudes, the BUV data in the early 1970s were significantly below the extrapolated trend line. We suggest that part of the northern mid-latitude trend of the 1980s through early 1990s was due to dynamical differences late in this period compared to earlier. This part of the trend would not extrapolate backwards yielding the result we observe.

Publications

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Near Real-time Assimilation in Support of Flight Planning for the SOLVE Campaign

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Research Objectives

We will produce assimilated winds and temperatures using the GEOS-2 Data Assimilation System (DAS) in near real-time for the duration of the SOLVE mission. Assimilated forecasts will be used in flight planning and the assimilated analyses will be used in post-flight data analyses. We will also use forecast winds to run a mountain wave forecast model, relevant to the goals of pilot safety and to flying Lagrangian flight tracks. Our assimilated products will be also used as meteorological input by three other SOLVE theory investigations for production of additional flight planning and data analysis products.

Summary of Progress and Results

The GEOS-DAS has provided the primary meteorological input for forecasting and flight planning for four recent ER-2 campaigns. GEOS-DAS forecast winds have also played an important role in previous missions by providing meteorological input for the Naval Research Laboratory Mountain Wave Forecast Model (NRL/MWFM, which was developed at NASA Goddard more than 6 years ago. Mountain wave forecasts are an essential flight planning tool because they help ER-2 pilots avoid hazardous mountain wave-induced turbulence.

Beginning 1 December 1999, we will produce near real-time stratospheric meteorological forecasts and analyses in support of flight and mission planning for the SOLVE mission. We will send an assimilation production person into the field for the first 1-2 weeks of each DC-8 and ER-2 deployment to make certain the assimilated products are customized to the mission scientists needs and available in a timely manner. We will also provide forecasts and analyses of mountain wave activity during the ER-2 deployment using the NRL/MWFM with GEOS-DAS winds. This is very important for SOLVE ER-2 flights, which will involve high-altitude flights over significant topography (e.g., Greenland, the Scandinavian ridge, and Iceland) in the remote polar environment.

Publications

None

Middle Atmospheric Hydrogen Photochemistry

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Research Objectives

The objectives of this research are to (1) investigate the chemical and dynamical processes which control the abundances of hydrogen species in the mesosphere and upper stratosphere; and (2) evaluate their role in the catalytic destruction of ozone. This research focuses on the use of global scale measurements of hydroxyl (OH) from the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) and coincident ozone (O_3) measurements from the Cryogenic Infrared Spectrometers and Telescopes for the Atmosphere (CRISTA) experiment, along with H_2O , CH_4 , and other data obtained from UARS HALOE (Halogen Occultation Experiment) observations. This work utilizes 1-D photochemical models to investigate fast acting HO_x chemistry which controls OH/ HO_2 partitioning and active oxygen loss in the mesosphere and upper stratosphere, along with 2-D chemical-dynamical models to study the chemistry and transport of long-lived tracers such as H_2O , H_2 , and CH_4 .

Summary of Progress and Results

(1) Comparison and analysis of MAHRSI OH data from both the November 1994 mission and the reflight in August 1997 has confirmed that the OH abundances in the mesosphere are significantly lower (30-40%) than that expected using standard photochemical theory. This result, along with independent ground based observations of lower mesospheric HO_2 and O_3 , strongly suggests that the rate coefficient of the reaction $O + HO_2 \rightarrow OH + O_2$ is lower (by 2 sigma) than the laboratory determined value. This has a major impact on our understanding of HO_x chemistry and the ozone budget in the upper stratosphere.

(2) Our study of HO_x chemistry, based upon the MAHRSI OH observations from both missions, has strengthened the view that OH is an excellent proxy for the abundance of H_2O (its source molecule). We have found that the observed distribution of OH in the mesosphere can only be explained by a layer of H_2O near 68 km altitude, and is completely consistent with the H_2O layer observed in that region by HALOE. However, our studies of the chemistry of the long-lived species H_2 , H_2O , and CH_4 has shown that the existence of this layer is directly counter to that expected by standard middle atmospheric chemistry and dynamics. We have developed a theory

that the H₂O layer is formed by surface chemistry on meteoric dust, and we are continuing to explore possible scenarios for O + H₂ surface kinetics in our modeling studies.

(3) As part of our coordinated campaign of space and ground based measurements during the second MAHRSI mission, we are collaborating with the THOMAS (Tera Hertz OH-Measurement Airborne Sounder) team which performed coincident OH column measurements taken in Europe during several MAHRSI overflights. Our model/data comparisons have shown that the MAHRSI and THOMAS OH observations in the upper stratosphere and lower mesosphere are in agreement that the observed OH is significantly lower than predicted by standard photochemical theory.

(4) The MAHRSI team has recently perfected the inversion technique to retrieve OH density profiles down into the upper stratosphere. The results show that below about 50 km altitude the observed OH increases rapidly with decreasing altitude to a peak near 43 km where the observed OH density is in fact larger than that predicted by the standard theory. Furthermore, the observed OH appears to be consistent with balloon-borne observations of OH extrapolated upward into the 40-50 km region. Taken at face value this strongly suggests that neither standard photochemical theory nor any previous proposed modifications can account for the OH distribution in the upper stratosphere and mesosphere.

Publications

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DC-8 Mission Support and Data Analysis

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Research Objectives

The goal of this project has been to design field missions involving the NASA DC-8 aircraft, carry out these field missions, and see that the data are archived and utilized. The TOTE/VOTE mission was carried out in December 1995 and January 1996. During this reporting period these data have been archived, and various members of the community have used them. Hence this mission has been fully completed. Subsequently we have been active in planning the SOLVE mission. It was originally planned that the mission would be flown in the winter of 1998/99. However, a delay in the launch of the SAGE III instrument caused the mission to slip to the winter of 1999/2000. Planning for this Mission is far advanced. Instruments have been selected, and flight strategies are being developed.

Summary of Progress and Results

During this period the data collected from the TOTE/VOTE mission have been made available to the community and the post-mission meetings have been completed. Planning has been carried out for the SOLVE mission. We have participated in a number of planning and review meetings for this mission. Strawman flight plans have been generated, and we have participated in all aspects of planning the mission that were appropriate.

Publications

This project has generated contributions to a number of planning documents such as the TOTE/VOTE and SOLVE Mission documents.

Mesoscale Exchange of Vortex Air

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Research Objectives

The processes which control the transport of air into and out of the lowermost regions of the polar vortex during winter are still not fully understood. Mixing estimates contain substantial errors, perhaps because the ubiquitous occurrence of vertically-narrow layers in the tracer fields (laminae in one dimension; tracer sheets in two-dimensions) along the vortex boundary, which are too small to be adequately represented by atmospheric models, are playing a significant role in the exchange of vortex and extra-vortex air. Tracer laminae are present throughout the winter, their numbers maximizing between 14 and 17 km at the vortex boundary during February. Aircraft, satellite and balloon-borne data will be employed to study the mesoscale exchange of air across the polar vortex boundary in the form of tracer laminae. The co-location of measurements from a number of different platforms will allow, for the first time, simultaneous observations of these features in two dimensions. The tracer, pressure and temperature profiles from SAGE III, if available, will provide valuable supplementary information in the regions where the aircraft fly, as well as elsewhere along the vortex boundary. The meteorological conditions prevalent during these observations will be used to initialize the University Corporation for Atmospheric Research (UCAR) mesoscale model, version 5 (MM5), to help identify the nature of the exchange mechanism(s). A prognostic global climate model (GCM) will also be used in an effort to follow the life-cycle of a number of laminae, using a PV-like tracer, provided the vertical resolution can be made sufficiently high to at least partially resolve them. In this way, the extent to which these processes represent an irreversible, meridional transfer of vortex air into mid-latitudes may be estimated. It is also hoped that the results will be useful for future model parameterizations, and in estimating the contribution laminae make to mid-latitude ozone values.

Summary of Progress and Results

October - December 1999 Activities: Peripheral software is under development to use with the UCAR MM5 model to study the mesoscale processes involved in tracer laminae generation.

January - March 2000 Activities: Ozone laminae appear each fall shortly after the polar vortex forms, becoming increasingly abundant as winter progresses and reaching a peak abundance during February and March. The ER-2 aircraft will fly in the middle of the vertical range occupied by these features, and extensive sampling is expected during the second and third phases of the SOLVE campaign.

Both Adrian Tuck and Stephen Reid will therefore be present in the field during phases 2 and 3, contributing as members of the theory team. Two Macintosh computers will be transported into the field to run Fractal and meteorological software, the latter to aid in mission planning in order to obtain the most suitable data for this project. The close temporal and spatial coincidence of numerous observation platforms during SOLVE should offer an unprecedented opportunity to study tracer laminae (in ozone, water vapor, nitrogen dioxide and aerosols) as they form, and every effort will be made to influence mission details to sample probable source regions for these phenomena.

April 2000 - March 2001 Activities: After a number of sensitivity tests, that the MM5 will be used to identify probable laminae generation processes, and enable an estimate of the exchange of air across the vortex boundary in the mesoscale range, previously impossible because of incomplete spatial and temporal data coverage. This result is expected to contribute towards an explanation of the observed changes in high-latitude winter ozone concentrations, providing a measure of the amount of air transported from the vortex on these smaller scales. In particular, it is anticipated that at least some of the discrepancy between models and observations, almost certainly arising from the incomplete representation of mesoscale processes in the former, will be explained.

The MM5 is a limited-area, non-hydrostatic, terrain-following sigma-co-ordinate model, and its function here will be to attempt simulations of the mesoscale and regional-scale atmospheric processes in the vicinity of the vortex boundary, where observations suggest laminae are forming. Model runs will span periods of a few days only since observations have already indicated that laminae form rapidly, on time-scales of just a few hours.

Whilst the MM5 is suitable for studying dynamical processes over a limited domain, it is not possible to use this model to study the evolution of laminae once they have formed. We therefore intend to use a prognostic global climate model to follow the evolution of these air masses as they are transported irreversibly into mid-latitudes. This work, not included in the original proposal, will be somewhat experimental since, at this stage, we are uncertain that the vertical resolution of the model can be sufficiently enhanced to capture these processes. However, we hope to be able to study at least one case where the laminae are particularly large in both the vertical and horizontal.

Publications

None

Mapping Antarctic Ozone from Visible-Channel Satellite Data

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Research Objectives

Accurate, detailed maps of total ozone were not available until the launch of the Total Ozone Mapping Spectrometer (TOMS) in 1978. However, the Scanning Radiometer (SR) on NOAA satellites during the 1970s included a visible channel that overlapped closely with the Chappuis absorption band of ozone around 600 nm. The Antarctic atmosphere and snow surface contain no other significant absorbers of radiation at those wavelengths, which makes Antarctica an ideal region to isolate the ozone signal in the visible-channel data, and offers hope of using SR data to map Antarctic ozone prior to 1978. A second objective, which turned out to be more successful, was to use the snow surface of the Antarctic Ice Sheet as a stable calibration target for visible channels on satellites.

Summary of Progress and Results

1. Calibration of the AVHRR Visible Channel Using Bidirectional Reflectance of Antarctic and Greenland Snow: The snow surfaces of the high plateaus of the East Antarctic and Greenland ice sheets were used to determine multi-year drift in the sensitivity of the visible channel of the AVHRR on the polar-orbiting satellites NOAA-9, 10, and 11. Bidirectional reflectance distribution functions are empirically derived for the months of October-February (Antarctica) and April-August (Greenland) using a simplified atmospheric model. The bidirectional reflectance of the snow surface should not change from year to year for near-nadir satellite views. Therefore, drift in the derived bidirectional reflectance distribution functions is interpreted as drift in channel sensitivity.

Several factors make the snow surface of an ice sheet suitable as a calibration target for visible and near-UV channels. (1) In this spectral region, snow has a very high albedo (>97%) that is invariant with grain size and incidence angle. (2) On the high plateaus the temperatures are always far below freezing so the surface consists of cold fine-grained snow, and there is negligible contamination. (3) The ice-sheet surfaces are uniform and flat across large areas. (4) Ozone is the only significant variable absorber in this spectral region, and its absorption can be accounted for if the ozone amount is known. (5) Cloud detection and removal is not necessary, because the thin clouds over the high ice sheets apparently do not alter the near-nadir reflectance, as they do over dark surfaces.

Our analysis indicates that the visible channel on NOAA-9 degraded linearly over the lifetime of the instrument (February 1985-October 1988) by $5.3 \pm 0.1\%$ per year. The change in sensitivity of channel 1 on NOAA-10 (December 1986-August 1991) was non-linear, but can be fitted well with a fourth-order polynomial. Data from NOAA-11 processed for November 1988-February 1991 (prior to the eruption of Mt. Pinatubo) showed a linear increase in sensitivity of $2.3 \pm 0.2\%$ per year.

2. Effect of Chappuis-Band Absorption and Bidirectional Reflectance of Snow on Reflected Radiance in AVHRR Visible Channel: Application to Remote Sensing of Total Column Ozone over Antarctica. Empirically derived bidirectional reflectance distribution functions (BRDFs) for the sub-ozone layer (snow, clouds, and Rayleigh scattering) were generated for 32 geographic gridboxes on the East Antarctic Plateau using radiances from the AVHRR in the 1980s. Absorption by ozone was accounted for using coincident total column ozone retrievals from TOMS. The derived BRDFs are used, along with the known Chappuis absorption coefficient of ozone and the sun/satellite geometry, to derive total column ozone over East Antarctica from AVHRR visible channel radiances. The method is tested for 1985-1986, when the results could be compared to those from TOMS. Error in derived ozone amount is lowest on the high plateau of East Antarctica and at solar zenith angles 65° - 80° . Errors for 5-day gridbox averages are typically 30 Dobson Units (DU), but sometimes exceed 100 DU. In its current state of development the method is therefore not accurate enough to justify its application to scanning radiometer data from the 1970s. The essential difficulty is that the Chappuis absorption signal is not large compared to unresolved spatial and temporal variability of the BRDF.

Publications

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Development of an Ozone Climatology from the Ground to 1 MB and Analysis of Interannual Variations of Stratospheric Transport of Ozone

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Research Objectives

Our first research objective was to develop a climatology for ozone from the ground to 50 km, based on measurements made at the surface, from balloons (ozonesondes) and from SAGE II (Stratospheric Aerosol and Gas Experiment). We required that the ozone climatology was consistent with ozone column measurements made by TOMS (the Total Ozone Mapping Spectrometer). Such a climatology is needed (1) for evaluation of stratospheric and tropospheric models, (2) in applications where it is necessary to specify an ozone distribution (e.g., climate models), and (3) to provide a-priori ozone profiles for retrieval algorithms for satellite measurements of ozone. Our second objective was to examine tracer transport in the stratosphere with emphasis on the distribution of exhaust products from a fleet of supersonic civil transport aircraft. The tool for this assessment was a newly developed interactive two-dimensional (2-D) model of the dynamics, chemistry, and radiation of the stratosphere. Our goal was to validate the model by comparing with observations of long lived tracers gathered by instruments aboard the Upper Atmospheric Research Satellite (UARS) and the Atmospheric Trace Molecule Spectroscopy experiment (ATMOS), as well aircraft data obtained during SPADE (Stratospheric Photochemistry, Aerosols and Dynamics expedition) and ASHOE/MAESA (Airborne Southern Hemisphere Ozone Experiment and Measurement for Assessing the Effects of Stratospheric Aircraft).

Summary of Progress and Results

1. Ozone Climatology: We initially developed a tropospheric climatology for ozone, for use in our calculation of the global distribution of OH. This climatology is 2-dimensional at middle and high latitudes, and 3-dimensional in the tropics, to allow for the large differences in ozone values over the Pacific and Atlantic Oceans. The vertical profiles are derived from ozonesonde data, and the 3-D distribution is based on the tropospheric ozone columns derived by Fishman and Brackett [1997]. The climatology is available on our web site. We provide a synthesis of what is known about the distribution of ozone in the troposphere and lower stratosphere, and

give recommendations for testing 3-D models of chemistry and transport with these data [Logan, 1999a, b]. We also used the sonde data to quantify the build up of ozone in the lowermost stratosphere of the Northern Hemisphere in winter, and its loss in late spring and summer [Logan, 1999b].

A preliminary stratospheric climatology was developed for use in NASA's Models and Measurement II activity (MM II), in collaboration with R. McPeters and G. Labow of NASA/Goddard. We derived the climatology for 1988-96 using ozonesonde data and SAGE II measurements. The SAGE II data were used above 20 km, based on the results of a detailed evaluation of the accuracy of the data using independent ozone measurements [WMO, 1998]. The sonde data were used for 0-30 km, and the profiles blended for 20-30 km. Monthly means were formed for each type of data in 10° bins for 80°N - 80°S , with 2 km resolution. The mean sonde and SAGE II profiles agree within 5-10%. The integrated profiles are also in excellent agreement with TOMS column data. We used the stratospheric climatology to evaluate 13 stratospheric models in MM II [Park *et al.*, 1999]. Most models agree with observations above 25 km, but there are major differences between many models and observations between 20 km and the tropopause, thought to be due to deficiencies in model transport.

2. Analysis of Stratospheric Transport: We find that our 2-D model can explain many of the characteristics of the observed distributions of long lived trace gases. The model uses a consistent formulation of advective and diffusive transport in the sense of residual circulation theory, assumes negligible large scale horizontal mixing in the tropics, and uses the full primitive equations to calculate mean meridional velocities in the tropics. Tropical confinement is reproduced by the model, and the mass exchange between tropics and mid-latitudes is consistent with measurements of the mean age of air and the propagation of CO₂ on a seasonal time scale into the tropics and mid-latitudes of the lower stratosphere [Schneider *et al.*, 1998a, b]. The sensitivity of the model results to changes in K_{yy} was examined and shown to be small. The only requirement for explaining observed correlations between CO₂ and N₂O is that the time scale for horizontal diffusion in the mid- and high latitudes of the lower stratosphere is shorter than a season. In addition, the model has successfully reproduced observations of the quasi-biennial oscillation (QBO) signal in ozone in the tropics and subtropics [Jones *et al.*, in preparation]. The meridional circulation associated with the QBO modulates the advective mass flow in the tropics and subtropics. The ability of the model to reproduce the ozone signal is a sensitive test for its simulation of tracer transport from the tropics to the mid-latitudes in the lower and middle stratosphere.

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Tropospheric and Stratospheric Composition Retrievals Using the Stellar Occultation Technique

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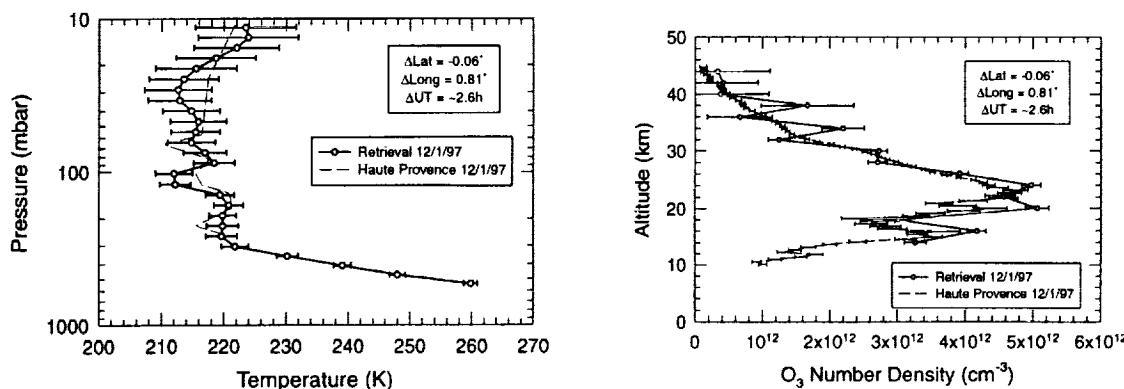
Research Objectives

The objectives of this program are to conduct a proof-of-concept study of a combined extictive and refractive stellar occultation technique for measuring stratospheric and upper tropospheric ozone and to develop the associated retrieval algorithms. Data from the Ultraviolet and Visible Imagers and Spectrographic Imagers (UVISI) onboard the Midcourse Space Experiment (MSX) satellite are being utilized to demonstrate this unique method for probing the composition and bulk properties of the stratosphere and upper troposphere and to conduct a preliminary validation of the scientific results.

Summary of Progress and Results

During June 1997-May 1998, we pursued the following activities:

- We developed an occultation technique which combines both refractive (observed by the UVISI visible imager) and extictive (observed by the UVISI spectrographic imagers) occultations. Measurements of atmospheric bulk density, pressure, and temperature inferred from the refractive occultation provided the critical Rayleigh extinction knowledge needed to improve the accuracy of lower atmospheric constituent densities retrieved from the extictive occultation observations. This technique and the associated retrieval algorithms were tested using data acquired under a variety of conditions (twilight, nightglow, auroral) and have proven viable in each case. We developed formulations for estimating the retrieval uncertainties using error propagation theory and confirmed these through rigorous Monte Carlo simulations. In conjunction with this work, we also carried out a detailed analysis of the uncertainties associated with MSX/UVISI data themselves.
- The improved retrieval algorithms were applied to observational data from several MSX/UVISI stellar occultations. We began preliminary validation of the MSX/UVISI results through a comparison of the retrieved temperature and ozone profiles to those obtained from sonde and lidar measurements at stations in Haute Provence (see figures), Eureka, and Lauder.



Example retrieved temperature and ozone profiles compared to ground-based measurements at the Haute Provence lidar facility

- A meeting was held at JHU/APL in August 1998 with members of the EnviSAT/GOMOS algorithm development team, headed by Dr. Errki Kyrola from the Finnish Institute of Meteorology. It was agreed that both sides would benefit from a sharing of knowledge, and arrangements were made for a collaborative comparison of analysis methods.
- A meeting was held at JHU/APL in February 1999 with our Russian colleague, Dr. Yuri Timofeyev, to discuss progress on our collaborative efforts. Issues related to the numerical uncertainties arising from standard refractive angle calculations were raised and discussed in detail. Dr. Timofeyev also presented preliminary results from the analysis of error sources and the optimization of the analysis algorithms being conducted by his team in St. Petersburg. After reviewing the current state of the occultation analysis and algorithm development, an outline for future work was developed.

Publications

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B 2. PREDOMINANTLY TROPOSPHERIC CHEMISTRY

Data-Based Climatologies of Chemical Constituents in the Free Troposphere and Lower Stratosphere

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Research Objectives

A number of fundamental questions remain in our understanding of the chemistry and dynamics of the upper troposphere and lower stratosphere, which can have significant impacts on our estimates of ozone depletion, radiative forcing and other factors leading to potential climate change. Global observations-based climatologies of photochemically important species and dynamical tracers could help answer some of these questions. Numerous measurements of chemical species and aerosols have been made throughout the troposphere and lower stratosphere, which we have compiled into "data composites" to be used in the evaluation of satellite measurements and global chemical transport models. All of the measurements are critically evaluated by studying the results of intercomparisons, as well as assessing our confidence in the measurement techniques used. These composites are made available to the scientific community by means of a website. Airborne-, balloon- and ground-based (non-urban *in situ* and remote) measurements are included in the compilations. In addition, data sets that have not otherwise been made publicly available will be added to the University of Michigan/SASS Data Archive and also included in the "data composites." Through the study and use of these data composites we will be able to gain a greater understanding of the global distributions of ozone, water vapor, aerosols and other trace species and their seasonal variations in the upper troposphere and lower stratosphere.

Summary of Progress and Results

Data composites of a number of chemical species important in ozone photochemistry have been created by gridding tropospheric aircraft measurements onto global maps. This work is an extension of the NO_x and NO_y "climatologies" we developed previously [Emmons *et al.*, 1997]. Currently composites are available for ozone (O₃), carbon monoxide (CO), nitric oxide (NO), NO_x (=NO+NO₂), NO_y (total reactive nitrogen), nitric acid (HNO₃), peroxyacetyl nitrate (PAN, CH₃CO₃NO₂), hydrogen peroxide (H₂O₂), methyl hydroperoxide (CH₃OOH), formaldehyde (CH₂O), acetone (CH₃COCH₃), ethane (C₂H₆), and propane (C₃H₈). The data have been compiled from a number of sources, including the NASA Global Tropospheric Experiment (GTE), Subsonic Assessment (SASS), and UARP campaigns, as well as International Global Atmospheric Chemistry (IGAC) and European campaigns. Numerous plots of the composites, as well as individual data files, are available from our website (<http://aoss.engin.umich.edu/SASSarchive/>).

Additional species will be added to the composites, including additional hydrocarbons (such as C₂H₂ and isoprene), alkyl nitrates, halocarbons, methane, water vapor, sulfur compounds (SO₂, DMS), and aerosol composition, size distribution and number density. Data from additional measurement campaigns will also be added as they become available.

These data composites have already been used for evaluation of a number of global chemical transport models. A preliminary evaluation of the Model for OZone and Related chemical Tracers (MOZART, version 1) developed at NCAR was presented in Hauglustaine *et al.* [1998]. Further comparison of MOZART results, along with results from IMAGES (Intermediate Model of Global Evolution of Species), to the data composites has led to further confidence in the results of the models in many [Emmons *et al.*, 1999]. Comparison of a number of species at one time has allowed for identification of areas that the models need improvement, such as that the NO_x emissions from biomass burning may be too low in MOZART. A number of other research groups have also made use of the composites for evaluation of their models (e.g., D. Rotman at Lawrence Livermore National Lab, D. Shindell and L. Grenfell at NASA/GISS, D. Wuebbles at Univ. Illinois/Urbana-Champaign, M. Lawrence at Max Planck Institute-Mainz).

Publications

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Tropospheric Chemistry Studies Using Observations from GOME and TOMS

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Research Objectives

To quantitatively determine trace gas and aerosol amounts from the Global Ozone Monitoring Experiment (GOME) and the Total Ozone Monitoring Experiment (TOMS) and perform chemical modeling studies which utilize these results. This includes:

- (1) Analysis of measurements from the GOME and TOMS instruments for tropospheric distributions of O₃ and H₂CO; tropospheric enhancements of SO₂, NO₂, and aerosols associated with major sources; and springtime events of elevated BrO in the lower Arctic troposphere.
- (2) Application of a global 3-dimensional model of tropospheric chemistry to interpret the GOME observations in terms of the factors controlling the abundances of tropospheric ozone and OH.

The goals of the proposed research are:

- (1) To determine global climatologies of trace species associated with ozone chemistry in the stratosphere and troposphere.
- (2) To better understand the role of transport from the stratosphere, export from polluted continents, and large-scale photochemistry in determining the abundances of tropospheric ozone.
- (3) To analyze changes in tropospheric chemistry associated with perturbing events, including volcanic eruptions, large-scale fires, and polar springtime halogen enhancements.
- (4) To use H₂CO as a photochemical tracer of OH chemistry and hydrocarbon reactivity in the troposphere.

Summary of Progress and Results

This is a relatively new program. We have concentrated as a first priority on the capability to retrieve H₂CO from GOME measurements in a stable fashion and with high precision. We are now able to do this, for the first time in the GOME program (preliminary studies, by the DLR and SAO allowed measurements of high pollution episodes). We are currently investigating the development and distribution of H₂CO emissions from Amazon and Indonesian biomass burning and from emissions by biogenic and anthropogenic sources over the North American continental boundary layer. SO₂ fitting studies are currently underway; volcanic SO₂ is routinely measured, and we expect to be able to measure SO₂ from anthropogenic pollution to high precision within several months.

Publications

None

Investigation of Tropical Tropospheric Water Vapor

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Research Objectives

Research performed under this proposal is focused on the regulation of water vapor in the tropical upper troposphere. This region is important for understanding many aspects of the Earth's atmosphere. Mass entering the stratosphere must transit this region, and the abundance of water vapor in the stratosphere is set primarily by processes occurring here. In addition, the cold temperatures in this region ($T < 200$ K) make the abundance of water vapor and other greenhouse gases in this region crucial for understanding the climate.

In particular, our research addresses two interrelated questions:

- What regulates the water vapor abundance of the tropical upper troposphere?
- What regulates the water vapor abundance of air entering the stratosphere?

Summary of Progress and Results

What regulates the water vapor abundance of the tropical upper troposphere? We have developed a simple trajectory model of the tropical upper troposphere that includes only advection and, whenever relative humidity exceeds 100%, condensation. Despite the simplicity of the model, the simulations agree well with measurements by the Microwave Limb Sounder (MLS) onboard the Upper Atmosphere Research Satellite (UARS). We see no evidence to suggest that accurate predictions of the humidity in this region are dependent on accurate simulations of microphysical processes nor on transport of ice or liquid water. Our results instead suggest that accurate predictions of the humidity primarily require realistic three-dimensional large-scale (> a few hundred km) wind fields. We have a manuscript describing these results [Dessler and Sherwood, 1999], which has been submitted to the *Journal of Geophysical Research*.

What regulates the water vapor abundance of air entering the stratosphere? Before understanding this overarching question, one must first answer a number of other questions. Among them: Where does air enter the stratosphere, and how much water vapor enters the stratosphere? We have worked on these two latter questions.

Until recently, it was generally believed that air enters the stratosphere in the western tropical Pacific, northern Australia, and Indonesia during the November to March period and over the Bay of Bengal and India during the monsoon; this theory has become known as the "stratospheric fountain" hypothesis. Using support from this grant, we reexamined this theory [Dessler, 1998]. We found that using more recent data on water vapor abundances and temperature, we could not eliminate zonally-averaged entry. Consequently, our analysis provides no support for the "stratospheric fountain" hypothesis.

Second, an analysis by Remsberg *et al.* [1996] used HALOE data to suggest that water vapor entering the stratosphere was 3.45 ppmv. This was about 10% lower than other estimates, and this disagreement caused some to suggest that our understanding of how much water vapor was entering the stratosphere was poor. Using support from this grant, we used a more recent version of HALOE data and redid the analysis [Dessler and Kim, 1999]. We found in our analysis that water vapor entering the stratosphere was 3.8 ppmv, in good agreement with other analyses.

Publications

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Further Studies of Tropospheric Chemistry Using Satellite Data

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Research Objectives

The objective of this research is to develop a methodology that can be used to determine the distribution of the integrated amount of ozone in the troposphere through the simultaneous measurements of total ozone from the Total Ozone Mapping Spectrometer (TOMS) and the integrated amount of ozone in the stratosphere from Solar Backscatter Ultraviolet (SBUV) satellites. However, as the research progressed, we discovered that the archived SBUV data are not in good agreement with climatological ozonesonde measurements in the troposphere and lower stratosphere. Thus, to implement this methodology, we have modified the SBUV data so that they can be used concurrently with available TOMS data. The resultant tropospheric ozone residual fields can then be used to provide insight into global tropospheric chemistry processes and also applied to specific case studies.

Summary of Progress and Results

Although our research group attained cursory success using TOMS and SBUV data to interpret the distribution of tropospheric ozone during the Transport and Atmospheric Chemistry Experiment—Atlantic (TRACE-A) mission in 1992, subsequent analysis of the use of these data [Vukovich *et al.*, 1997; Ziemke *et al.*, *JGR*, 103, 1998] showed that there were inherent problems with the use of SBUV data in the lower stratosphere and upper troposphere. Thus the initial phase of our research during this period focused on an extensive examination of the distribution of ozone derived from the archived SBUV data and a comparison of these data with more than 20 stations that have launched ozonesondes.

As a result of these analyses, a new technique for determining the integrated amount of ozone in the troposphere using concurrent observations from SBUV and TOMS data was developed and then compared with various data sets. The technique makes use of the SBUV observations in the lowest three levels (1013 mb-63 mb) of archived SBUV data to construct a climatology that is consistent with ozonesonde measurements. In the lowest layer (1013 mb-253 mb), where ozone is almost always tropospheric, the SBUV measurements do not recreate the seasonality found in the ozonesonde data and consistently underestimate the amount of ozone at northern middle latitudes, the latitudes of interest for a regional application used for testing this methodology. On the other hand, a significant positive finding in the SBUV/ozonesonde analysis is that the

integrated ozone amounts between 1013 mb and 63 mb determined from SBUV are in good agreement with both the seasonality and the absolute ozone amount determined from the ozonesonde profiles. This result can then be used for determining a more accurate quantification of how much ozone is in the both the troposphere and the stratosphere from any specific SBUV measurement. When used in conjunction with concurrent total ozone measurements from TOMS, we obtain better information about the distribution of ozone in the troposphere using the tropospheric ozone residual (TOR) technique. The TOR are then computed for the eastern United States during 1988 and compared to the ozonesonde measurements from Wallops Island during that year. The resultant comparison between the TOR and the Wallops Island measurements is considerably better using this technique when compared to calculated TOR values when the SBUV data are not corrected. The methodology is then applied to determine the large-scale daily distribution of tropospheric ozone during times when surface concentrations of ozone were unusually high over vast regions on the eastern United States.

Regional TOR patterns have been analyzed in conjunction with various meteorological data sets and satellite imagery. Using such analyses, the relationship between the TOR distribution, meteorological processes in the lower troposphere, and the distribution of ozone at the surface during the 1988 episode has been examined. The regional distribution of the TOR is associated with the distribution of air masses that have evolved from the prevailing meteorological synoptic situation. The highest amounts of TOR are generally found off the coast of North Carolina and are consistent with the accumulation of ozone that had its origins over the northeastern United States and was subsequently advected southward off the North Carolina coast. The high TOR over the ocean is then caught in the persistent anticyclonic circulation at this particular time; subsequently, it becomes a source of ozone for the southeastern United States at a time when that region experiences numerous instances of surface ozone concentrations in violation of the EPA hourly standards. When, over a period of several days, the dominating high pressure system over the eastern U.S. breaks down, TOR values decline, consistent with the fact that cleaner air of tropical origin is transported into the region. Ongoing studies include the use of this technique to re-examine the generation and transport of ozone during TRACE-A and to examine and to quantify the amount of ozone produced from widespread biomass burning in Mexico in May 1998.

Publications

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Analysis of ATMOS Upper Tropospheric Trace Gases

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Research Objectives

Objectives for this research task are to vertically extend the analyses of the Atmospheric Trace Molecule Spectroscopy (ATMOS) high-resolution infrared solar absorption spectra to regions in the upper troposphere. Analyses of these spectra, acquired during four Space Shuttle missions, produce volume mixing ratio profiles of several key constituents in the stratosphere and upper troposphere, however, previous versions of the ATMOS data set did not extend below the tropopause. Current efforts have the goal of retrieving and analyzing vertical volume mixing ratio profiles for gases which are important in regulating tropospheric ozone and/or are useful tracers of surface sources, such as NO, NO₂, HNO₃, H₂O, CH₄, CO, C₂H₂, C₂H₆, and HNO₄.

Summary of Progress and Results

Previous results of ATMOS reported in the literature ("Version 2") were generated using an onion-peeling algorithm. While efficient, this approach was not reliable for tropospheric retrievals. During 1997 and 1998, work centered on adapting more robust but computationally lengthier "global-fitting" retrieval software for use with the ATMOS spectra. These efforts also included a complete re-evaluation of ATMOS processing methods to better exploit the capabilities of the global-fitting algorithm. Re-processing of the spectra was begun in 1998, and a new "Version 3" data product was completed in the first quarter of 1999. Version 3 results compared favorably with previously reported Version 2 results in the stratosphere and lower mesosphere, and were significantly more reliable for tropospheric retrievals. In addition, the Version 3 data set showed greater stability for upper stratospheric/lower mesospheric gases such as CO and NO. Preliminary comparisons with other tropospheric data sets (e.g., SONEX, PEM-West-A) showed similar correlations for tropospheric source gases (e.g., C₂H₂ vs. CO). Comparisons with satellite-based instruments (e.g., HALOE and MLS) were also favorable when taking dynamical variability into account.

In collaboration with Dr. A. Eldering (JPL) and Dr. M. Newchurch (U. Alabama at Huntsville), a new addition to the Version 3 results has been the retrieval of extinction or absorption bands of aerosols. This involves the removal of known line and broadband absorption features of trace gases to leave the residual broad aerosol absorption. Preliminary retrievals of stratospheric sulphate aerosol profiles have been obtained, with good agreement with results from SAGE.

Consultations with the ATMOS science team were made on a regular basis, and the team had a meeting in May 1999 to review the new Version 3 data set, and discuss related scientific investigations. Several works-in-progress using the new data set were presented: general overview (M. Gunson, JPL); data consistency and integrity (F. Irion, JPL); Cl and F budgets (R. Zander and E. Mahieu, U. Liège); aerosol retrievals (A. Eldering, JPL; F. Mills, UCLA; M. Newchurch and D. Bowdle, U. Alabama at Huntsville); upper stratospheric NO and CO (C. Rinsland, NASA Langley); water, methane and CO₂ isotopomers (Y. Yung and E. Moyer, Caltech); use of ATMOS data in photochemical modeling (R. Salawitch and G. Osterman, JPL; M. Prather, UC Irvine); tracer analysis, polar vortex and extra-vortex chemistry (H. Michelsen, Sandia National Labs, CA); and dynamics and tracer/active species instrument retrieval intercomparisons (G. L. Manney, now at New Mexico Highlands University).

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Direct Measurements of Tropospheric Ozone from TOMS Data

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Research Objectives

The objective of this research is to investigate the retrieval of tropospheric column ozone directly from the TOMS measured radiances. The initial investigation was limited to the tropics for the years 1991 and 1992. It was shown that tropospheric column amounts could be derived which were in good agreement with in-situ ozone sonde measurements. The technique developed for these two years were then applied to the entire TOMS data set, from 1978 through 1992. An extension of the technique is currently applied to the real-time EP TOMS radiances, and these results are shown on a Department of Meteorology home page (<http://metosrv2.umd.edu/~tropo/>). We have also investigated what the variance of the total ozone is as a function of latitude in the Northern Hemisphere. We have found that if we sort the archived total ozone results by meteorological regimes defined by the upper tropospheric fronts (north of the polar front, between the polar and subtropical fronts, and south of the sub-tropical front), then the total ozone and the ozone profile are quite homogeneous within each regime. Thus we can fix the stratospheric profile for each regime. We have applied this fact to the derivation of tropospheric ozone during severe pollution events along the East coast.

Summary of Progress and Results

The method for deriving time-averaged tropical tropospheric ozone, developed by Kim [1996] (Kim, J. H., R. D. Hudson, and A. M. Thompson, *JGR*, **101**, 24317-24330, 1996) was refined and applied to a 2-year period, 1991 to 1992. This period was selected because of the availability of a series of ozone sonde measurements made at Natal, Ascension Islands, and Brazzaville. These measurements were used to normalize the tropospheric ozone values derived from the TOMS radiances. Comparison of the sonde data and the TOMS derived data clearly showed that the wave one pattern, observed in the tropical ozone record to have its maximum over the South Atlantic, was due to two factors, one being the predominance of biomass burning in South America and Africa, the other a persistent wave one pattern independent of the biomass

burning. The amplitude of the latter was found to have a semiannual periodicity with a minimum in June and December.

As an extension to this study, we assumed that the magnitude of the periodicity of the persistent pattern derived, using the sondes as truth, could be extended to other years. The first year studied was 1990, for which mid-Atlantic ozone sondes were also available. Using the wave-one parameters derived from 1991-1992 we were able to get excellent agreement with the 1990 sonde measurements. We then extended the analysis to the entire period of the TOMS Nimbus-7 data set. A paper giving details of this analysis is in press.

The technique has also been applied to real-time EP-TOMS data, and the derived ozone field is posted on an ozone home page (<http://metosrv2.umd.edu/~tropo/>). It should be stressed that the data set is for the tropics only.

If one examines the archived Gridded Total Ozone product in the tropics at a given latitude, then a plot of the total ozone versus longitude reveals a wave pattern, the period of which matches the orbital period of the spacecraft. The maxima of these waves occur when the instrument is looking in the nadir direction, while the minima occur when the instrument observes the earth at the largest scan angles. We have found that this wave pattern is due to the fact that changes in tropospheric ozone from the profiles assumed in the look-up tables, are not retrieved as efficiently as similar changes in the stratospheric profile. In addition, this efficiency is a function of the optical depth, being less at the higher scan angles. We have shown that if one could observe the same point on the ground at different angles then one could derive tropospheric ozone using the measured radiances alone. The contribution function for the derived ozone is strongly weighted in the troposphere, with a peak at about 800 mb altitude. The basis for the method is described in a thesis by M.-Y. Ahn.

The stratospheric column ozone is remarkably constant in the tropics, and we have examined its constancy at higher latitudes. We have found that if one sorts the total ozone by meteorological regime, i.e., north of the upper tropospheric polar front, between the polar front and subtropical front, and south of the sub-tropical front, rather than by latitude, then the total ozone has a variance similar to that found in the tropics. High ozone events along the Eastern US seaboard, are the result of high pressure regimes which move the sub-tropical front to high latitudes. Not only is the stratospheric column constant throughout this region, but so also is the stratospheric ozone profile. We have developed an algorithm which makes use of these facts to retrieve tropospheric ozone on a daily basis.

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A Climatology of Tropospheric CO over the Central and Southeastern United States and the Southwestern Pacific Ocean Derived from Space, Air, and Ground-Based Infrared Interferometer Spectra

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Research Objectives

We propose to develop a climatology of tropospheric carbon monoxide (CO) for the central and southeastern United States and southwestern Pacific Ocean using tropospheric CO retrievals from archived infrared spectra acquired by air- and ground-based interferometers. The quality assured climatological database will be made publicly available to the scientific community for model and measurement comparison and validation. We will employ appropriate trajectory analysis techniques for in-depth interpretation of a few selected cases. Where the data permit, we will investigate CO interannual variability in our climatological data. The primary dataset for this study is the 50,000+ spectra from 114 flights of the University of Wisconsin's (UW) High-resolution Interferometer Sounder (HIS) infrared interferometer. Although most HIS flights have been over or near the continental United States, seven 1994 HIS flights were over the extreme southwestern Pacific between New Zealand and the Antarctic. These seven flights will provide CO climatology, permit intercomparison with observations from the Measurements of Atmospheric Pollution from Space instrument, and enable investigation of the impact of the south polar vortex on tropospheric CO distributions. In addition to the HIS spectra, we will retrieve boundary layer CO from the archived spectra of the UW ground-based, portable Atmospheric Emitted Radiance Interferometer (AERI) and the Department Of Energy (DOE) Atmospheric Radiation Measurement Program (ARM) Cloud and Radiation Test Facility (CART) AERI in Oklahoma. Many HIS flights overflew at least one AERI thus enabling lower

tropospheric CO profile retrievals. Nearly two years of continuous CART AERI spectra provide characterization of boundary layer CO at this likely Earth Observing System validation site. We will employ our previously validated existing CO retrieval algorithm developed for NASA's Atmospheric Infrared Sounder. However, we will investigate the development of CO profile retrieval algorithms for the AERI data. Our comprehensive analysis of the HIS and AERI archives will provide a unique and invaluable climatological database to the tropospheric chemistry modeling and observing community.

Summary of Progress and Results

Major project milestones since funding began in March 1998, include: the addition of Dr. Hui He as Research Associate, streamlining and semi-automation of CO retrievals from AERI spectra, detailed analysis of AERI spectra acquired during the First Pre-launch MOPITT (Measurement Of Pollution In The Troposphere) Validation Exercise (Pre-MOVE), and the beginning of the CART AERI CO climatological database with initial analysis of spectra from February to September 1998. Planned activities for the remainder of FY99 and FY00 include: development of an AERI Fast Model required for timely analysis of the full AERI spectra archive, automation of HIS CO retrieval algorithm for processing HIS spectra archive, and completion of National Polar orbiting Operational Environmental Satellite System (NPOESS) Aircraft Sounder Testbed (NAST) CO retrieval algorithm for processing the burgeoning archive of NAST spectra.

Pre-MOVE at the Southern Great Plains DOE ARM CART site was successfully accomplished the first week of March 1998. Our analysis of Pre-MOVE AERI spectra has been presented at two meetings of the MOPITT Correlative Measurements Team, published in *The Earth Observer* [Wang *et al.*, 1999], and presented at meetings of both the American Geophysical Union [McMillan *et al.*, 1999a] and the Optical Society of America [McMillan *et al.*, 1999b]. We find the total tropospheric CO columns retrieved from AERI spectra agree within 10% with total column CO measurements retrieved from high-resolution grating and interferometer spectra acquired coincidentally at the CART site. Pre-MOVE commenced the important and necessary task of validating AERI CO retrievals. Currently, a detailed analysis of AERI spectra acquired during the Second Convection And Moisture EXperiment (CAMEX-2) with coincident aircraft CO profiles is underway. All available AERI CO retrieval validation results are planned for publication submission later in 1999.

A detailed analysis of tropospheric CO column densities retrieved from the AERI spectra during Pre-MOVE (March 2-4, 1998) shows synoptic variations with time [He *et al.*, 1999a, b, and c]. A substantial increase in CO column density coincided with a marked decrease in surface pressure and a surface wind changing from westerly to southerly to easterly, indicating passage of a warm front. Prior to this event, the CO column was rather constant under the influence of northerly and westerly winds. Thus, the CO column changed as the origin of the air masses over the CART site changed [He *et al.*, 1999a, b, and c].

The seven month time series (February to September 1998) of AERI CO retrievals from the CART site exhibit additional synoptic variations with additional diurnal variations evident at some times. Data processing continues to fill out the rest of the year 1998. We even see signs of the CO seasonal cycle in the background values, lower in late summer and higher in late winter, in general agreement with previous measurements of CO seasonality over the United States. The

most striking feature in this time series is the appearance of extremely large enhancements in tropospheric CO during May 1998. These CO enhancements coincide with enhanced aerosol concentrations observed by satellite and CART site instruments and correlated with transport of smoke plumes from extensive biomass burning in Mexico and Central America [He *et al.*, 1999d].

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Derivation of Tropospheric Ozone Climatology and Trends from TOMS Data

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Research Objectives

This research addresses the following three objectives: (1) Derive tropospheric ozone columns from the TOMS instruments by computing the difference between total-ozone columns over cloudy areas and over clear areas in the tropics. (2) Compute secular trends in Nimbus-7-derived tropospheric ozone column amounts and associated potential trends in the decadal-scale tropical cloud climatology. (3) Explain the occurrence of anomalously high ozone retrievals over high ice clouds.

Summary of Progress and Results

Several methods have been developed to extract information about the tropospheric ozone distribution. The tropospheric ozone residual method [Fishman *et al.*, 1996, 1990] suffers from uncertainty in the lower-stratospheric ozone amounts in SAGE and SBUV. Tropospheric ozone derived from TOMS alone with some stratospheric ozone assumption [Kim *et al.*, 1996] suffers from the uncertainty in the assumption. Topographic contrast method [Jiang and Yung, 1996; Kim and Newchurch, 1996, 1997] suffers from limited spatial coverage. Therefore, we investigate the Convective Clouds Differential (CCD) method [Ziemke *et al.*, 1998] to compute reliable, self-consistent tropospheric ozone amounts, and derive tropospheric ozone trends.

Anomalous high or low ozone amounts over clouds will affect the application of CCD method. We locate ozone anomalies based on spatial correlation between reflectivity and ozone in the TOMS L2 data. There are both positive anomalies and negative anomalies (correlation coefficient between ozone column and 380-nreflectivity and reflectivity is greater than 0.5 or less than -0.5, respectively). The frequency of occurrence of ozone anomalies is about 25% between 60° north and 60° south. A significant fraction of these cases, especially in mid-latitudes, is due to real, geophysical correlation between ozone and the pressure systems associated with clouds.

Positive anomalies in middle- and high-latitude regions peak in summertime for both hemispheres and are lowest in wintertime. Positive anomalies in the tropics peak from August to October, coincident with the biomass burning season. Negative anomalies peak in summer and fall, are lowest in winter and spring. The slope between ozone and reflectivity for those anomalies increases with latitude, especially in wintertime.

For most of the negative anomalies, there is good positive correlation between ozone and the difference between the International Satellite Cloudy Climatology Project (ISCCP) and Temperature Humidity and Infrared Radiometer (THIR) cloud top pressure. The cloud climatology error contributes significantly to the formation of negative anomalies. For most of positive anomalies, ozone is not well correlated with the cloud pressure difference. The increase of retrieval efficiency of lower tropospheric ozone with reflectivity mainly contributes to the formation of positive anomalies in biomass burning regions.

There are ozone retrieval errors due to cloud height and radiance interpolation errors for high reflectivity clouds, which are used to derive the stratospheric ozone using the CCD method. Therefore, we developed a correction scheme to correct ozone above clouds by using TOMRAD (the forward model) and TOMS V7 inversion algorithm. We also developed another scheme for correcting total ozone column due to cloud-height error.

The total ozone column consists of two parts: stratospheric ozone and tropospheric ozone. The total ozone column is the fundamental TOMS product, and stratospheric ozone is equal to the ozone above cloud whose top is at tropopause level. Therefore, tropospheric ozone is derived by subtracting this stratospheric ozone over high clouds from the total column ozone. This method was first developed by Ziemke *et al.* [1998].

In order to use the CCD technique to derive tropospheric ozone, we need a pair of points, a clear point and a high cloud point (CCP). CCP includes two cases: (a) In case one, CCP refers to two points, where one is a clear point and the other is a high cloud point, with the points located near to each other in one day's measurement. (b) In case two, CCP refers to two points, one clear point and one high cloud point, in two successive days' measurements at the same geographical location. Due to the natural occurrence of clear and cloudy regions meeting these criteria, the minimum time required to construct a global map of tropospheric ozone (with some missing areas) is three days.

Tropospheric ozone at CCPs is derived by subtracting the ozone column at a high cloud point from the ozone column at a clear point. If several CCPs exist for a certain point, the point having the minimum THIR cloud pressure is exploited. For regions without clouds reaching tropopause, CCP is unavailable there. Although we can get the total column ozone from a clear point, the stratospheric ozone can not be calculated directly like that at points with CCP. In the Ziemke *et al.* [1998] study, zonal invariance of stratospheric ozone is assumed to solve this question, however our study shows that the stratospheric ozone features a clear longitudinal wave-one pattern.

Three primary error sources affect the CCD method are (1) Interpolating zonal stratospheric ozone over missing data areas will cause 2-3 DU error in the final result; (2) reduced efficiency of TOMS in detecting the variability of the lower tropospheric ozone [Hudson, 1995], approximately 1-3 DU, additional error is introduced to the CCD method; and (3) the capability of identifying clouds with tops at the tropopause level with TOMS data, roughly additional 3-5

DU errors are added. Assuming that the three errors are independent, the total error is the root sum square of the three errors. Then the local 2σ measurement errors are ~7 DU, on average.

Monthly mean tropospheric ozone distributions shows that the south Atlantic area is a high tropospheric ozone region, while the India ocean and the west Pacific Ocean is a low tropospheric ozone region. The tropospheric ozone at the east Pacific Ocean varies annually.

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Use of MAPS, GTE, and UARS-MLS Data in Understanding Tropospheric Processes Critical to Model Development

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Research Objectives

Two of the major problems in using meteorological models to explain observed tropospheric trace constituent distributions and thereby to understand the global budgets of the tracers are to properly define the layered structure in the free atmosphere, and to properly represent the transfer of material from the boundary layer to the upper troposphere and vice versa. We proposed to tackle these problems through the examination of an extensive collection of trace constituent data from research and commercial aircraft in conjunction with meteorological data from the European Center for Medium-Range Weather Forecasts. The physical mechanisms responsible for these advection and layering processes will be explored and their implications for model fidelity will be assessed. In addition, we will estimate the effects of thin layers (not currently resolved by models) on the net photochemical production/destruction of species due to nonlinear reaction rates.

Summary of Progress and Results

We developed an improved algorithm for trace constituent layer detection [Stoller *et al.*, 1999], and used it to analyze over 100,000 km of ozone and humidity vertical profiles collected by instruments piggybacked on commercial aircraft [e.g., Cho *et al.*, 1999a]. The same method was also used to examine ozone, humidity, carbon monoxide, and methane data from the NASA Pacific Exploratory Missions [Stoller *et al.*, 1999]. The major conclusions from these studies were that tropospheric trace constituent layers are ubiquitous, and that their characteristics are remarkably universal [Newell *et al.*, 1999]. For example, approximately half of the layers were of the high-ozone/low-humidity type, regardless of season or geographical region. Because the combination of tracer concentration anomalies that define these layers can be used as markers for their origins (e.g., a high-ozone/high-humidity layer would likely have been raised by convection from the polluted boundary layer), we can study the importance of layer formation to vertical tracer transport. This work is ongoing, with potential vorticity being used as an additional marker. The nonlinear effects of layers on photochemical production/destruction is also currently being investigated.

We have also performed radiative heating/cooling calculations on some observed layer structures, and have demonstrated that the sharp edges on humidity layers can have strong local effects of self-stabilization (dry layers) or destabilization (wet layers), and have suggested that clear-air turbulence might result from the latter case through convective instability [Stoller *et al.*, 1999; Newell *et al.*, 1999].

We put a “microscope” on one particular kind of layer (tropopause fold) and used fine-scale *in situ* measurements plus data from an ozone lidar and microwave temperature profiler to study the instabilities that led to stratosphere-troposphere ozone transfer [Cho *et al.*, 1999d]. We observed both convective instability from breaking gravity waves and Kelvin-Helmholtz instability from wind shear. The former type appears to be an important source of 3D turbulence that had previously not been considered for tropopause folds.

We also systematically analyzed the mesoscale variabilities, not only of the trace constituents, but also of the aircraft-measured dynamical variables [Cho *et al.*, 1999b]. We learned that, in the free troposphere over the ocean, vortical modes and/or quasi-2D turbulence dominated in nonequatorial latitudes, while gravity waves were more prevalent in the equatorial region [Cho *et al.*, 1999c]. One of the implications of this result is that the characteristics of horizontal tracer advection should be different for the two latitudinal regions, and that the possibility of inverse energy cascade in the extratropics makes subgrid parameterization of models more difficult.

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Tropical Tropospheric Ozone from Satellite, Sondes and Airborne Missions: Data Product Development and Analysis

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Research Objectives

Three types of activities fall under this project: (a) foremost is the development of tropospheric ozone products from TOMS; (b) interpretation of daily, seasonal and interannual ozone variability deduced from satellite and sondes; (c) related analysis, modeling and assessment activities with Goddard, University of Maryland, and other colleagues in the US and internationally. Modeling has included investigations with M. Chin (Georgia Tech.; [Chin *et al.*, 1998]) on global sulfur and interpretation of ice and snow data with J. McConnell (University of Arizona, [McConnell *et al.*, 1998]).

Summary of Progress and Results

Three milestones were achieved in the derivation of tropical tropospheric ozone from TOMS, building on and modifying the method developed during the previous three years' funding cycle. First, the technique of using averaged (13-16 days) Level 2 TOMS total ozone with its wave-one pattern and a climatology of ozonesondes to differentiate tropospheric and stratospheric ozone was generalized for the period 1991-1992 [Hudson and Thompson, 1998]. In contrast to Kim *et al.* [1996], it was assumed that the wave-one pattern (more ozone over the eastern Atlantic than at 180 degrees longitude by 10-40 DU) is in the troposphere, which is consistent with sondes and the satellite observations from SAGE and UARS/MLS and HALOE. The resulting tropospheric ozone column was compared to the Ascension, Brazzaville, and Natal (Brazil) sondes during the pre-TRACE-A and TRACE-A periods to show that the method for 1991-1992 was accurate within 5 DU. We termed the wave-pattern-sondes technique for retrieving tropical tropospheric ozone (TTO), the "modified-residual" method.

Second, an annual periodicity was found in an underlying background amount of tropospheric ozone at 0 degrees longitude, which suggested that the modified-residual method could be applied to other years. The 1991-1992 cycle in tropospheric ozone (at 0 degrees longitude) was used to initiate processing real-time Earth-Probe/TOMS and ADEOS/TOMS data in early 1997. These maps can be viewed with daily orbits, and as averages over the previous 3 and 9 days.

This work is performed by students and the website is at: <http://metosrv2.umd.edu>. An archive of maps for the full ADEOS period and all EP/TTO maps (1996-) is available on the homepage. These maps allowed us to follow Indonesian fires during the El- Niño-related fires in late 1997 [Thompson *et al.*, 1998] and South American fires in 1998 during the CLAIRE (Coordinated LBA Airborne Experiment, a Max-Planck Institute [Mainz]-Brazilian effort).

The third milestone was application of the modified-residual method to the 14 complete calendar years of Nimbus 7/TOMS, averaged in 2 maps/month at 1 degree latitude and 2 degree longitude resolution (20N-20S, maximum coverage). These data are available at the website http://metosrv2.umd.edu/~tropo/14y_data.d. Evaluation and validation of the N7 and EP/TTO maps was made with MLS, SAGE ozone and with Atlantic region sondes. An important result embedded in the N7/TTO times-series is that no trend was found throughout the tropics for the period 1980-1990. A paper on the evaluation and trends, with the announcement of the public release of the N7 data is in press [Thompson and Hudson, 1999].

With the development of the modified-residual and other methods for deriving tropical tropospheric ozone from satellites, the scarcity of independent ozone data for validation became critical and has been addressed by the SHADOZ (Southern Hemisphere Additional Ozonesondes) TOMS-funded project in 1998-1999 [Thompson and Witte, 1999]. Weekly ozonesonde data from 10 Southern Hemisphere tropical sites is being collected at a single archive http://hyperion.gsfc.nasa.gov/Data_services/Shadoz/shadoz_hmpg2.html. Analysis of this data has begun, along with ozonesonde observations from campaigns of opportunity that are also in SHADOZ. The Aerosols-99 oceanographic cruise of the *R/V R H Brown*, collected 25 sonde profiles. These are being studied to determine factors affecting the tropical-subtropical ozone transition and dynamical-chemical interactions at the tropics [Fall 1999 AGU: Doddridge *et al.*, 1999; Johnson *et al.*, 1999; Thompson *et al.*, 1999].

Studies of tropical ozone over Brazil during SCAR-B [ozonesondes during the "Smoke, Clouds And Radiation - Brazil," 1995; Longo *et al.*, 1999; Kaufman *et al.*, 1998; Remer *et al.*, 1998], of boundary layer ozone over Reunion Island [Bremaud *et al.*, 1998] and of persistent ozone layers at Pretoria, South Africa [Tyson *et al.*, 1997] took place during the past three years. These papers used observations taken by SHADOZ co-investigators. It is expected that joint scientific studies will help maintain these sites and lead to continued collaboration with colleagues in tropical countries.

Review and assessment-related activities from this project: Hansen *et al.* [1997] (Thompson, co-author); Thompson *et al.* [1997]; Olson *et al.* [1997] (Thompson, co-author); Lelieveld and Thompson [1999].

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Stable Isotopes and Radiocarbon in Atmospheric Methane and its Sources

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Summary of Progress and Results

Beginning September 1, 1995 and continuing to January 31, 1999 we received funding from NASA. We conducted a measurement and modeling program aimed at understanding atmospheric CH₄ and its sources and sinks. We continued our bi-weekly monitoring of CH₄ mixing ratio, δ¹³C, and ¹⁴C content at the mid-continent remote background air site at Niwot Ridge, CO (begun in January 1989) and added bi-weekly measurements of CH₄ and its δ¹³C value at a coastal Northern Hemispheric site at Montaña de Oro State Park, CA (begun in July 1995). The California site is close to the terminus of a trans-Pacific shipping lane running between Los Angeles, CA and Auckland, New Zealand. Through a collaboration with Dr. David Lowe of NIWA in New Zealand and the Blue Star Shipping Lines (now P & O Shipping, Ltd.) we began analyzing CH₄ in air samples collected approximately twice yearly from shipboard air sampling. We also obtained upper air samples from NASA-GTE and NASA SONEX aircraft collections through a collaboration with Professors Don Blake and F. S. Rowland at University of California, Irvine. Data from these samples along with published data in other studies were used in modeling studies we conducted. For example, we used a 2-D tropospheric photochemical tracer transport model to help explain the abrupt changes in CH₄ mixing ratio growth rate in the period from 1989-1993 and to study kinetic isotope effects in CH₄ loss processes and the atmospheric CH₄ budget. More recently, we used the 2-D model to investigate our measurements of atmospheric methane for the period 1994 to 1996. The magnitude of the observed isotopic shifts in atmospheric CH₄ with altitude were examined using model calculations and experimentally determined values for carbon kinetic isotope effects (KIEs) in chemical loss processes of CH₄.

We have also used our NASA award to study the atmospheric chemistry of CH₄ with respect to its reactions undergoing KIEs. In a theoretical study, we calculated the carbon kinetic isotope effect in the gas-phase reactions Cl or OH + CH₄ → HCl + CH₃ using standard Hartree-Fock methods with help from Professor Max Wolfsberg and Dr. Mike McGrath (both of University of California, Irvine). A need arose for this because of difficulty in reconciling the observed atmospheric CH₄ isotopic signature with what is known about CH₄ sources and sinks from other measurement data, theoretical calculations, and laboratory determined measurements of the KIE of CH₄ loss processes. Basically, upper atmospheric values of CH₄ are more enriched with respect to surface values by an amount much larger than can be explained on the basis of published KIEs in the reactions of CH₄ with OH and Cl. In an experimental study, we worked

with scientists at the University of California at Riverside (Professor Roger Atkinson and Dr. Ernesto Tuazon) to measure the KIEs of C and H in the reaction of CH₄ with Cl within a controlled laboratory reaction cell. This reaction is extremely important in atmospheric CH₄ isotope chemistry because while reaction with OH is the principal sink for CH₄, reaction with Cl appears to have a much larger KIE. Our result, along with recent determinations by two other research groups (one theoretical and one experimental), indicate convergence toward consensus values for both the C and H KIEs in this reaction. Our manuscript is in preparation.

As promised, we were able to investigate specific CH₄ sources and sinks through a combination of the NASA award above and extramural funding (such as an award from the USDA to study CH₄ production and oxidation in rice paddies). Using primarily NASA funds, we studied high latitude lakes in Siberia with an eye toward establishing another remote air sampling site in the lake region and conducted a study of the kinetic isotope effect in the atmospheric reaction of CH₄ with Cl. Using primarily USDA funds, we investigated biogeochemical factors controlling production, oxidation, and release of CH₄ in rice paddies. In paddy fields along the Gulf Coast of Texas (in collaboration with Professors Ron Sass and Frank Fisher of Rice University), we studied factors which control CH₄ production and oxidation using isotope measurements of C and H. A principal finding was our strong evidence that rhizospheric CH₄ oxidation occurs in paddy fields and the development of a method to calculate the per cent of CH₄ oxidized as a function of total CH₄ produced from field measurements of δ¹³CH₄ under natural conditions. The partitioning of CH₄ production from bacteria using either methyl group fermentation or CO₂ reduction with H₂ has also been calculated using isotopic data.

Publications resulting from the NASA proposal cited here and from extramural funding used in projects directly related to our NASA proposal are listed below.

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Study of Tropospheric Ozone and UV Reflectivity Using TOMS Data

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Research Objectives

Our principal objectives are: (1) study of tropospheric ozone using TOMS data, and (2) study of UV reflectivity of the Earth using TOMS data. We will relate the time history of the changes in tropospheric ozone to their probable causes (e.g., biomass burning, industrial activity) using the meteorological data archived by the Goddard Space Flight Center (GSFC) Data Assimilation Office (DAO). Using TOMS UV reflectivity data, we will carry out an independent and rigorous test of the impact of the solar cycle on clouds. This work is in response to the recent claim by Svensmark and Friis-Christensen [1997] that they found, using the International Satellite Cloud Climatology Project (ISCCP) cloud data, a correlation of a large variation (3-4%) in global cloud cover with the solar cycle. We propose to do two things: (a) confirm the ISCCP results using TOMS reflectivity data in the seven years when the data overlap, and (b) extend the test for correlation using TOMS data over one full solar cycle.

Summary of Progress and Results

Our interest in the hydrological cycle motivated us to study the interannual variability of clouds in the TOMS (Total Ozone Mapping Spectrometer) reflectivity data. This is an example of how a global data set that is primarily obtained for atmospheric composition (O_3) may be used for climate studies. Other experiments may provide more information but only TOMS can make a unique and singularly important contribution to the temporal pattern of change. Based on a detailed analysis of the cloud data obtained by the International Satellite Cloud Climatology Project (ISCCP) in the years 1984-1990, we conclude that cloud variation during a solar cycle is not simply a 3% variation in cloudiness as reported by Svensmark and Friis-Christensen [1997]. In fact, this variation consists of two distinct components for optically thin and optically thick clouds. The solar cycle variation of thin cloud amount (optical depth smaller than 9.38 in the visible) is 6% and is in phase with the cosmic rays flux while variation of thick cloud amount is 3% and has the opposite phase as the cosmic rays flux. The total cloud variation is about 3%, in agreement with previous study. We argue that galactic cosmic rays increase the cloud amount by producing ions that enhance cloud nucleation when there are no clouds, or when the clouds are thin. However, in thick clouds, enhanced cosmic ray flux could accelerate the coalescence growth of water droplets, thus inducing precipitation and reducing the total cloud amount.

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B3. PREDOMINANTLY AEROSOLS AND RADIATION

The Use of POAM II and SAM II Aerosol Extinction in an Investigation of the Climatology and Morphology of PSCs

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Research Objectives

The Naval Research Laboratory's Polar Ozone and Aerosol Measurement II and III (POAM II and POAM III) instruments are space-based visible/near infrared photometers for making measurements of stratospheric constituents (ozone, aerosol extinction, water vapor, and NO₂) in the solar occultation mode. They are similar in instrument concept and measurement capability to the NASA SAGE II instrument. However, the POAM instruments are in a sun synchronous polar orbit and, thus, provide continuous measurements over the polar regions of both hemispheres. Therefore, they are uniquely well suited to study of polar stratospheric clouds (PSCs). POAM II was launched in September 1993, and provided measurements until the host SPOT 3 satellite failed in November 1996. POAM III was launched on the SPOT 4 satellite in March 1998, and the instrument is now in routine operation. The primary research objective of this study is to use the POAM data to produce and maintain a climatology of PSCs in both hemispheres, and to make this climatology publicly available to the scientific community. A second objective is to use the POAM data to investigate PSC morphology, specifically PSC composition and formation scenarios.

Summary of Progress and Results

POAM II was in operation for the Northern Hemisphere PSC seasons of 1993-94 through 1995-96, and the 1994-1996 Southern Hemisphere PSC seasons. We have developed [Fromm *et al.*, 1997] and refined [Fromm *et al.*, 1999] a POAM PSC detection algorithm. We have used this

algorithm to produce a catalog of PSC observations for both hemispheres. This catalog contains the altitude and intensity of each PSC, along with information about temperature at the location of the PSC, and its position with respect to the vortex. In addition, we have developed a technique using the POAM data to distinguish Type II PSCs using a model of the POAM instrument, and a PSC microphysical model. Briefly, we have found that Type II PSCs are associated with extinctions that distinguish them from the range of extinctions reflective of Type I PSCs made up of either nitric acid trihydrate (NAT) or supercooled ternary solutions (STS). The range of extinctions likely with NAT and STS clouds are sufficiently low that POAM II can always resolve these clouds as it sweeps through the atmospheric limb. However, Type II clouds are opaque to the POAM tracking mechanism, so the resultant abnormally high termination of a POAM measurement event is indicative of the presence of Type II clouds. This information has been added to the POAM PSC catalog. This catalog is publicly available through the NRL web site. We have also published a climatology of PSCs for the years of POAM II operation for both the Northern and Southern Hemispheres [Fromm *et al.*, 1997, 1999].

We have adopted the POAM II PSC detection algorithm and catalog to POAM III. The POAM III experiment is currently operational, and thus far the instrument has monitored the 1998 and 1999 Southern Hemisphere PSC seasons, and the 1998-1999 Northern Hemisphere season.

Publications

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SBUV/2 and SSBUV Solar Spectral Irradiance Data Analysis

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Research Objectives

The solar ultraviolet (UV) irradiance is the major driving force behind the chemistry and dynamics of the Earth's middle atmosphere. Therefore, measurements of the solar UV spectral irradiance and its variations are needed for photochemical studies and to understand the thermal structure, dynamics, and energy budget of the terrestrial atmosphere. The Solar Backscatter Ultraviolet/model 2 (SBUV/2) series instruments on NOAA satellites have made near daily solar irradiance measurements since 1985. The Shuttle SBUV (SSBUV) instrument made regular solar irradiance measurements, 1989-1996. The goal of this research is to establish a multi-SBUV instrument, long-term solar spectral irradiance data set and to use these data to assess solar UV spectral irradiance change. There are three specific objectives. The first objective is to understand and reduce the biases between the absolute UV solar spectral values reported by the various instruments. The second objective is to use SSBUV as a long-term calibration standard for the NOAA-9 and NOAA-11 SBUV/2 data sets and to determine daily values of the solar irradiance for the period 1985-1998. The third objective is to compare the SBUV-series solar irradiance measurements with predictions of a facular model of solar UV activity. These efforts will enhance our understanding of the solar UV irradiance change, and will supply information necessary to quantify the impact of solar variations on the earth's middle atmosphere.

Summary of Progress and Results

The most significant accomplishment of this research was the creation, validation, and distribution of the NOAA-11 SBUV/2 middle UV solar irradiance data set for the period 1989-1994. Regular underflights of the Space Shuttle SBUV instrument, SSBUV, were used to determine time and wavelength dependent NOAA-11 instrument sensitivity changes. The resulting NOAA-11 SBUV/2 solar spectral irradiance data product, which is available via the World Wide Web (URL listed above) and via anonymous ftp, has a long-term accuracy of better than $\pm 1\%$ at most wavelengths. Detailed analysis of the NOAA-11 solar data set was performed.

Both short and long-term changes were readily seen at most wavelengths. From 1989 to late 1994, the solar irradiance decreased by 3% between 215 and 250 nm. At 200-205 nm the solar irradiance decreased during this period by approximately 7%. Longward of 300 nm, no solar variations were observed to within the accuracy of the data. The long-term solar irradiance changes observed by the NOAA-11 SBUV/2 instrument were compared with corresponding data obtained by the Solar-Stellar Irradiance Comparison Experiment (SOLSTICE) and Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) onboard the Upper Atmosphere Research Satellite (UARS). The solar variations measured by the three experiments are in reasonable agreement. In particular, the SBUV/2 and SUSIM measurements of long-term solar variations agree with one another (and with predictions of a Mg II index proxy model) to within approximately 1%. The SOLSTICE data have moderate overall agreement, but the SOLSTICE observations were found to disagree with the other two instrument's observations and model predictions by roughly 2% or so in the 260 to 300 nm region. This suggests a small, uncorrected drift in the SOLSTICE data set in this region.

In the past year we began comparisons of the NOAA-11 SBUV/2 data with preliminary Nimbus-7 SBUV data. Although separated by roughly a decade, the two data sets cover similar portions - the extended maximum and declining phase - of their respective solar cycles. We are presently working to correct the Nimbus-7 data for long-term drift. In parallel to that effort, we are performing detailed statistical analysis of the Nimbus-7 and NOAA-11 data. We find similar evolution of short-term solar variations, although the NOAA-11 data generally have larger power spectrum values, suggesting a less complex frequency distribution of short-term activity during solar cycle 22 with respect to solar cycle 21. We are continuing to investigate whether these differences are physical in origin or an artifact of uncharacterized Nimbus-7 sensitivity change.

We are presently extending the long-term calibration technique developed for NOAA-11 to the NOAA-9 data. This analysis will be completed in late 2000.

Significant analysis of the absolute solar spectral irradiance in the middle UV was also performed. In particular, SSBUV data were compared to corresponding data from the two UARS solar spectral irradiance sensors and with data from two additional instruments flying on the Space Shuttle. The mean ratio of the UARS solar irradiance to the average Shuttle sensor-based irradiance was 1.0014 ± 0.0020 (2σ) and no spectral bias was observed. Instrument-to-instrument differences were somewhat larger, and our analysis indicates that it is now possible to measure middle and near UV solar spectral irradiance to an absolute accuracy of about 5%. This represents a factor of two to four improvement over the absolute accuracy previously obtained.

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GOME Data Analysis

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Research Objectives

We have extended the techniques and algorithms used in the analysis of the discrete wavelength backscattered ultraviolet radiance data from TOMS to the continuous spectral data from the ESA GOME instrument. The primary focus is on total column ozone retrievals. Recently, methods have been developed to compare other geophysical parameters such as tropospheric aerosol optical depths derived from backscattered ultraviolet measurements.

Summary of Progress and Results

GOME Introduction: The ESA GOME instrument, on ERS-2, was successfully launched in the spring of 1995. Although the GOME instrument uses the same backscatter ultraviolet physics as the SBUV/TOMS, it uses a different instrumental configuration. The GOME instrument has continuous spectral coverage from 240 nm to 810 nm, at two spectral resolutions. 0.2 nm (240-400 nm) and 0.4 nm (400-800 nm) resolution compared with six TOMS wavelengths (312-380 nm). The GOME instrument scans across the satellite track in three pixels. Each across track pixel has with a nominal ground resolution of 40 km (along) x 320 km (across).

Satellite Total Ozone Comparisons: We have used the NASA/Goddard Space Flight Center algorithms for calculation of the total column ozone using GOME radiance and irradiance data. This ozone product will be referred to as GOME-TOMS. This processing was done to check the GOME radiance/irradiance calibration and to test the systematic assumptions in the ESA DOAS algorithm. GOME-TOMS will not replace the ESA ozone processing. There is overall reasonable agreement between the GOME-TOMS and the GOME-DOAS. The GOME-DOAS results are consistently lower than the GOME-TOMS results and lower than the EP-TOMS results. GOME-DOAS has a 10% seasonal difference from EP-TOMS and GOMETOMS. The same seasonal difference is not observed in the GOMETOMS – GOME DOAS comparisons.

We have applied the long-term radiance degradation techniques that were developed for the TOMS instruments to the GOME instrument. No wavelength dependent degradation from (331 to 380 nm) was observed. An absolute degradation of 7% over 3 years was observed. This analysis is consistent with the degradation in the polarization monitoring device observed by Tanzi *et al.*, [ESAMS '99]. The GOME total ozone studies are ongoing. ESA views the GOMETOMS/GOME-DOAS comparisons as critical validation steps in the acceptance of the GOME total ozone data. Results were presented to ESA at the ESAMS '99 - European

Symposium on Atmospheric Measurements from Space, ESA ESTEC, in January 1999 Biomass Burning Smoke using GOME Hyperspectral Data.

A recently developed method for monitoring biomass burning smoke from space has been applied to measurements over Brazil. Long term measurements of aerosol index measured from space by a series of satellites show the inter-annual variability of smoke covered areas over Brazil. Using a newly developed algorithm, the aerosol index has been inverted into aerosol optical depth values. Coincident ground-based sun photometer aerosol optical thickness measurements are used to validate this inversion. The inter-annual variability of the area covered by smoke of varying intensity is described over the period 1978 to 1995. The size of the interannual changes dominate the long-term data record. Trends in absolute amounts of smoke coverage are not calculated because of small calibration shifts in the satellite data record and inter-satellite spatial coverage and calibration differences, but significant trends in smoke area coverage are not obvious in the data. Based on the 1995 GOME data, it appears that for overall smoke area coverage the SCAR-B mission occurred during a year that was similar to recent years, but the area covered by heavier smoke in 1995 was larger than other years in the data record.

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Theoretical Studies of Processes Affecting the Stratospheric and Free Tropospheric Aerosols

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Research Objectives

This research project had several objectives which were all related to the properties of aerosol particles in the stratosphere and free troposphere. Specific research tasks were (1) to develop a simple microphysical model suitable for modeling the Pinatubo plume and to study sulfate particle formation in a volcanic plume; (2) to carry out studies and assist in the analysis of sun photometer measurements; (3) to carry out studies to aid in the analysis of wire impactor data, and (4) to carry out theoretical studies including analysis of particle formation mechanisms for sulfate and nitric acid particles, the formation of nitric acid over the winter pole and the possibility that tropical cyclones are a source for stratospheric particles.

Summary of Progress and Results

Modeling studies included the development of a box model that includes all relevant microphysical processes affecting sulfate aerosols in the atmosphere. We have developed a parameterized nucleation scheme that we are planning to use in the model, and we are working on a heteromolecular growth process that can be easily incorporated into large models, such as the CARMA model developed at NASA Ames Research Center. We have also shown that for extreme conditions, such as encountered in a volcanic plume, the nucleation process can be described as the coagulation of small molecular clusters containing only one or two sulfuric acid molecules.

We have been involved in studies of the data obtained by the NASA Ames Sun photometer. A part of the analysis has been to consider how to incorporate new values for vapor pressures and optical parameters in the studies of the optical properties of sulfate aerosols as a function of environmental conditions such as temperature, relative humidity, etc. Another part of this analysis involved analyzing the ELSIE program that is widely used in the aerosol community to determine aerosol extinction from impactor data or from a given aerosol size distribution. We were able to show that the technique used by ELSIE to evaluate indices of refraction lead to values that are not consistent with laboratory studies of sulfuric acid solutions.

Work has been performed to analyze and interpret results obtained with the Ames Wire Impactor and other particle measuring instruments on NASA aircraft. We compared extinctions calculated from the number of particles on the wire with those measured by SAGE. The results indicate a persistent discrepancy between the two instruments. We are also using a simple box model to

evaluate observations made during the SONEX mission. This model indicates that some of the particle concentration measurements can be explained by the nucleation of sulfuric acid droplets.

We have carried out a number of theoretical studies involving aerosol particles. We have been working on a new approach to the formation of NAT particles in polar stratospheric clouds. Some interesting and promising preliminary results have been obtained. Another problem involves the layer of enhanced nitric acid that appears at high altitudes over the poles during winter. We have carried out modeling studies that show the layer can be explained by heterogeneous reactions on sulfuric acid droplets. We considered the possibility that tropical cyclones are a source for the background stratospheric aerosol layer. Studies carried out during the STEP program showed that ascending air associated with tropical cyclones is injected into the stratosphere. The temperature of this air is also cold enough to explain the extreme aridity of stratospheric air.

Publications

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Aerosol Measurements from TOMS

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Research Objectives

The objectives of this research program are to determine the characteristics, frequency of occurrence, and distribution of aerosols (dust, smoke, volcanic ash, and pollution aerosols) over the entire Earth. The data source for this study is primarily from TOMS (Total Ozone Mapping Spectrometer), with additional information derived from ground-based sun photometers (AERONET) and other satellites (GOME, AVHRR, SeaWifs, and Polder). The characteristics of interest are primarily optical depth, single scattering albedo, and aerosol plume height. The data obtained from use of TOMS data are compared with other satellites and ground-based information for validation.

Summary of Progress and Results

The first published studies of aerosols from TOMS data were focused on simply detecting their presence and determining whether they were in one of two categories (1) UV-absorbing aerosols (dust, smoke, volcanic ash); and (2) UV-non-absorbing aerosols (some forms of industrial pollution such as sulfates). The incidence of smoke over South America from the widespread biomass burning in Brazil (jungle and farmland clearing) was easily detected using the change in spectral contrast between two observing channels, 340 and 380 nm. At the same time, results were published that derived the frequency of occurrence for aerosols over the entire globe. The study showed the major locations of annual biomass burning in Africa and South America, and the largest source of dust in the atmosphere arising from a broad region stretching from the Sahara to India (10° – 30° N). The dust plumes are remarkable for the large areas covered, particularly over the Atlantic Ocean reaching as far as the Caribbean, Florida, and Central and South America. One of the principal results of these studies was the finding that the UV technique can detect and quantify the amount of aerosol over all types of surfaces (land, water, and snow/ice).

Once the location and seasonal cycles of the aerosols were established, algorithms were developed to derive the UV optical depth and single scattering albedo (absorption). These properties were directly compared to ground-based measurements from sun photometers and to the results from other satellites. The dust distributions were used to estimate the amount of

radiative forcing that contributes to additional atmospheric heating. It was also shown the boreal fires originating in Canada and Russia can spread smoke over a wide region. Smoke plumes were tracked from Canada over Greenland and shown to compare well with ice-core data.

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Antarctic Ultraviolet Radiation Climatology from the Total Ozone Mapping Spectrometer

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Research Objectives

The goal of this project is to develop a method by which total column ozone abundances and top-of-atmosphere ultraviolet reflectances measured by NASA's Total Ozone Mapping Spectrometer (TOMS) can be used to map the distribution of biologically active solar ultraviolet radiation (UVR) throughout Antarctica. The major challenge here lies in the wavelength coverage of the TOMS instrument (several ultraviolet wavelengths only). At ultraviolet wavelengths, clouds scatter solar radiation conservatively. As a result, it is very difficult to distinguish clouds from the underlying snow and ice surfaces that persist throughout the Antarctic. At ultraviolet wavelengths, the radiance contrast between cloud tops over ocean, and most sea-ice or snow cover, is too small for effective discrimination. Also, the TOMS footprint is too large to allow imaging of scene texture, which can sometimes be useful for cloud discrimination. If clouds cannot be reliably detected, then a radiative transfer model used to map surface UVR will not be able to include the strong multiple reflection effects between the high-albedo surfaces and the cloud base. In this case, maps of surface UVR will be highly inaccurate. Several other unique Antarctic satellite data sets, archived at the Scripps Institution of Oceanography's Arctic and Antarctic Research Center (AARC), will be brought to bear on this problem. Advanced Very High Resolution Radiometer (AVHRR) data will be used to detect cloud cover over sea and glacial ice, and Special Sensor Microwave Imager (SSM/I) data will be used to map the extent of sea-ice. Both retrievals will be co-located with Earthprobe TOMS data to better understand the TOMS-measured radiances. With such a robust empirical understanding of how the TOMS radiances are influenced by the underlying polar scene types, a remote sensing algorithm can be adapted for the Antarctic to map UVR over both the continent and Southern Ocean.

Summary of Progress and Results

The extraction and reduction of the AVHRR and SSM/I data, and their co-location with the Level 2 and Level 3 TOMS data, are straight-forward but time-consuming processes. We anticipate that if the data can be reduced covering the sunlit period of one full year in the Antarctic (1997, for comparison with the latest Earthprobe TOMS data), we will have several thousand pixels for intercomparison, which should be sufficient for all of our objectives. We are co-locating AVHRR, SSM/I, and TOMS data for three regions that are well-covered by the AARC's satellite data archive:

- (1) The "King George Island" region, latitudes 60-63 degrees south and longitudes 53.5 to 67 degrees west.
- (2) The "Palmer Station" region, latitudes 64-68 degrees south and longitudes 60 to 75 degrees west.
- (3) The "Siple Station" region, latitudes 70-77 degrees south and longitudes 75 to 85 degrees west.

These regions together give us a sample of all of the major geographic scene types that occur throughout Antarctica, including the marginal ice zone, ice shelves, and high plateau areas.

The data extraction, reduction, and co-location tasks for this project include (1) determination of which archived SSM/I and AVHRR overpasses will cover the desired regions, during sunlit periods, such that the SSM/I image can give a good estimate of sea-ice under the AVHRR image; (2) extraction, earth-location, and calibration of SSM/I and AVHRR data from the raw digital telemetry stored on DAT tapes; (3) cloud masking at 1-2 kilometer resolution using the AVHRR channels 3 and 4 (near and middle infrared), and estimating cloud fraction throughout the AVHRR images; (4) retrieval of total sea-ice concentration from the SSM/I brightness temperatures, using the NASA (GSFC) Team Algorithm developed for this sensor; and (5) extracting TOMS-measured radiances, total ozone, scene reflectivities, and estimates of cloud fraction from the TOMS Level 2 archive, and co-locating these pixels with the nearest AVHRR and SSM/I imagery.

As of this report, we are half way through the data set we have set aside for this project. We anticipate completion of this data processing by the end of calendar year 1999. Preliminary analysis of the processed and co-located data reveal inconsistencies between cloud fraction determined (reliably) from the AVHRR infrared channels, and cloud fraction estimated from the TOMS data using GSFC's mid-latitude algorithms. We also see the expected insensitivity in backscattered ultraviolet radiance to cloud amount, over higher albedo surfaces. After the principal investigator returns from field work in Antarctica (early February, 2000), detailed statistical and radiative transfer analysis will take place to determine (1) over what Antarctic conditions TOMS data can be used alone to map surface UVR, and (2) what ancillary satellite data are required over the more difficult higher-albedo surfaces. This research program was formulated in collaboration with Dr. Jay Herman (GSFC), and we will be in regular contact with his group as we make progress.

Publications

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Aerosol Retrievals from ATMOS Solar Occultation Spectra

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Research Objectives

The Atmospheric Trace MOlecule Spectroscopy (ATMOS) sensor observed over 400 solar occultations during one or two-week missions on the Space Shuttle in 1985, 1992, 1993, and 1994. ATMOS provides high-resolution ($\sim 0.01 \text{ cm}^{-1}$), broadband (4750-625 cm^{-1}), vertically-resolved measurements of limb transmittance spectra from the middle stratosphere to the upper troposphere. Narrowband analyses of the archived spectra have already provided valuable information on many atmospheric trace gases. However, broadband analysis of the same spectra has provided comparatively little information on atmospheric aerosol and cloud particles, primarily due to broadband radiometric uncertainties in the observed spectra. The objective of this research is to develop, validate, and employ an autonomous algorithm that retrieves the concentration, composition, and (possibly) size of aerosol or cloud particles from the ATMOS spectra, with minimal interference from the current broadband uncertainty.

Summary of Progress and Results

Development of an objective quantitative particulate retrieval algorithm for ATMOS requires fundamental improvements in five basic areas:

1. Ground-based processing of the observed signal spectra;
2. Broadband radiometric calibration spectra for limb transmittance;
3. Correction for line and continuum gaseous absorption;
4. Particulate complex index of refraction spectra versus composition and temperature; and
5. Accurate, computationally efficient particulate retrieval algorithms.

We began funded research work on these issues in April 1998, in conjunction with ongoing work by the Jet Propulsion Laboratory and the ATMOS Science Team. JPL researchers have concentrated on issues 3 and 5. Our work to date has concentrated on issues 1, 2, and 4, where we have employed several unconventional analytical methods. Two papers are in preparation on these tasks, with additional papers to follow.

Signal Processing and Calibration: We developed an implicit observation equation for the ATMOS spectra, and conducted an extensive radiometric error analysis on this equation, to account for solar variability, atmospheric refraction, receiver nonlinearity, unknown normalization constants, and other miscellaneous effects. The implicit equation involves a calibration coefficient that relates the archived spectral signal ratio (the endoatmospheric signal at a given frequency and tangent altitude, ratioed to the exoatmospheric signal at the same frequency, where both spectral signals are normalized by the largest signal in the corresponding spectrum) to the traditional transmittance ratio (the corresponding ratio of the endoatmospheric transmittance to the exoatmospheric transmittance). In this form, the calibration coefficient can exhibit significant variability and uncertainty. We renormalized the implicit observation equation using the signals from optimally located frequencies in each spectrum. We restructured the resulting equation by moving the exoatmospheric transmittance from the transmittance ratio to the calibration coefficient, and moving the endoatmospheric transmittance at the normalization frequency from the calibration coefficient to the transmittance ratio. The resulting calibration coefficients are almost always very close to unity; this result substantially simplifies particulate retrievals from ATMOS. We also began to evaluate the calibration uncertainty when endoatmospheric spectra are ratioed by adjacent spectra, instead of the traditional ratioing by exoatmospheric spectra.

Particulate Optical Constants: We conducted a theoretical and empirical study of infrared optical properties for common constituents in atmospheric aerosols and clouds, in order to develop a computationally efficient parameterization for these properties. We modified the observation equation to express particulate properties in terms of either mass or volume extinction coefficient (extinction cross-section per unit mass or volume), instead of the traditional extinction cross-section. We reviewed the rapidly growing laboratory database on infrared spectra for the particulate complex index of refraction and developed informal data exchange collaborations with several major laboratories that use flowing aerosols or supported thin films to conduct state-of-the-art research on these fundamental optical properties. We compared measured and modeled extinction spectra for pure artificial aerosols to measured extinction spectra from ATMOS. More recently, we examined the information content of particulate extinction spectra as a function of size and frequency, and estimated the sensitivity of that information content to changes in particulate composition and temperature. We showed that size information is much more apparent when the particulate extinction spectra are ratioed to the bulk extinction spectra for the corresponding particulate composition. We also began to study the information content and the information coding in truncated series for Fourier and Laplace transforms of particulate extinction spectra.

Publications

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SAGE II Aerosol Studies

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Research Objectives

The objectives of this research are to: (1) use principal component analysis to study the information content and particle size sensitivity of SAGE II multi-wavelength aerosol measurements; (2) develop optimal techniques for retrieving aerosol physical properties such as surface area density; and (3) use the retrieved parameters to develop global aerosol climatologies.

Summary of Progress and Results

Two significant studies of stratospheric aerosols using SAGE data were completed under this research task. The first study compared stratospheric aerosol loading measured by SAGE I in 1979 and by SAGE II in 1989-1991 [Thomason *et al.*, 1997a]. These periods are often termed background (non-volcanic) periods because aerosol levels were lower than at any other times in the modern measurement era with the exception of the present. Results show that the 1- μm aerosol optical depth in 1989-1991 was 10% to 30% higher (depending on latitude) than that observed in 1979. SAGE II data demonstrate that the latter period (prior to the June 1991 eruption of Mt. Pinatubo) was characterized by a continuing global recovery from the eruptions of El Chichon in 1982 and Nevada del Ruiz in 1985, with a further complication introduced by the February 1990 eruption of Kelut. The slow decrease of aerosol loading in mid-northern latitudes in 1989 and 1990 was most likely the combined result of the continuing loss of aerosol from the stratosphere following these volcanic injections and variations in the transport of aerosol from the tropical reservoir associated with the phase of the quasi-biennial oscillation. Therefore, the increase in aerosol loading between 1979 and 1989-1991 cannot be completely attributed to anthropogenic sources such as aircraft sulfur, as had been suggested by several earlier papers. The second study [Thomason *et al.*, 1997b] presented a global climatology of stratospheric aerosol surface area density derived using the multi-wavelength aerosol extinction measurements from SAGE II for the period 1984-1994. The spatial and temporal variability of aerosol surface area density at 15.5, 20.5, and 25.5 km were presented, as well as cumulative statistical distributions (median, 10-percentile, and 1-percentile) as a function of altitude and latitude. The time period encompasses the injection and dissipation of the aerosol associated with the June 1991 Mt.

Pinatubo eruption, as well as the low loading period of 1989-1991. During this period, aerosol surface area density varied by more than a factor 30 at some altitudes. Surface area densities derived from SAGE II and from the University of Wyoming optical particle counters were compared for 1991-1994 and were shown to be in generally good agreement. An extended climatology was also derived using single wavelength aerosol measurements by the Stratospheric Aerosol Measurement (SAM) II (1978-1994) and SAGE I (1979-1981) instruments. Aerosol surface area densities derived from the SAM/SAGE data record have been used to parameterize aerosol-catalyzed heterogeneous chemical processes in several model studies of global and polar ozone loss [Portmann *et al.*, 1996; Solomon *et al.*, 1996, 1997, 1998].

Publications

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Developing and Validating an Aerosol Model for the Upper Troposphere

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Research Objectives

The main focus of this proposal was to develop and validate an Aerosol Physical Chemistry Model for the upper troposphere. With this model we have calculated the following quantities: (1) the equilibrium partitioning of various species between the gas and aqueous phases for a wide variety of environmental conditions; (2) the variation in the inorganic aerosol composition as a function of temperature and relative humidity; (3) the solution compositions at which inorganic salt precipitation might occur in upper tropospheric aerosols; and (4) the deliquesce relative humidity (in the atmosphere this is the ambient relative humidity at which a completely dry aerosol becomes thermodynamically unstable and will transform into an aqueous solution droplet) of ammoniated and/or nitrated aerosols under upper tropospheric conditions. Predicting the equilibrium partitioning has important applications for both gas and aqueous phase chemistry modeling calculations, while the determination of aerosol composition and salt precipitation can play a significant role in predicting the frequency of cirrus cloud occurrence in the upper troposphere. In addition dry salt particles are in many cases transported into upper troposphere by convection and therefore it is important to predict whether such dry particles would deliquesce after being subjected to upper tropospheric temperatures and relative humidities. It is essential to determine the phase of the background particles which exist in the upper troposphere since the barrier to ice formation by vapor deposition on dry salt surfaces is significantly higher than that of homogenous freezing from aqueous solution droplets. Under this work we have investigated in detail the role of aerosol composition and phase transformation in nucleation and growth of cirrus clouds. We further plan to use the aerosol model, the aerosol compositional data obtained during SUCCESS, and air mass trajectories to examine whether the ice saturation barrier to nucleate cirrus clouds would vary in air masses which have different origins and histories. We have coupled the aerosol model to Ames' cirrus cloud model and ran several simulations assuming different compositions for the background aerosols to investigate how changes in aerosol composition affects the microphysical properties of cirrus and their subsequent radiative impacts.

Summary of Progress and Results

The presence of ammonium ion in upper tropospheric aerosols can greatly affect the mode of cirrus cloud formation. Using a mixed-electrolyte model of the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{NH}_3/\text{H}_2\text{O}$ system developed under this project three distinct solution neutrality and HNO_3 uptake regimes are

identified for the ice freezing process from the above solution. For solutions that are highly acidic (contain very little ammonium ion), the HNO_3 uptake has a small impact on the ice freezing process, except under conditions for which the HNO_3 mixing ratios are unusually high (>1 ppb) due to transport of regional polluted boundary layer air into the upper troposphere. In contrast, for partially neutralized aerosols such as NH_4HSO_4 , while the HNO_3 uptake still remains relatively small, salt crystallization readily occurs in solution, forming letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ cores that are embedded in an aqueous solution. For aerosols that are increasingly neutralized to compositions near the $(\text{NH}_4)_2\text{SO}_4$ system, the strong HNO_3 uptake by the particles will result in the accumulation of H^+ ions and subsequent crystallization of either letovicite or mixed double salts of ammonium nitrate with ammonium sulfate in solution. Thus for most cases (unless the ammonium ion concentration is extremely low in solution), the presence of ammonium ion in upper tropospheric aerosols will enhance cirrus formation by altering the mode of ice nucleation from homogeneous to heterogeneous freezing nucleation due to formation of mixed-phased particles.

Combining the results of aerosol/cloud model calculations with aircraft field observations, we have found that ammonia and/or HNO_3 pollution in the upper troposphere can have a strong impact on the cirrus formation process and chemistry in the upper troposphere. Our preliminary studies suggest that contrary to common belief, transported material from regional air pollution to the upper troposphere, rather than aircraft exhaust, are primarily responsible for the observed change in the high cloud cover. Thus the tripling of Asian air pollution in the future should have a strong and measurable impact on cirrus cloud cover in the next few decades with important applications for global climate change. In addition, we have found that upper tropospheric aerosols that contain basic components (i.e., dust and/or biomass), and not cirrus, are primarily responsible for trace gas partitioning and therefore condensed phase chemistry in the upper troposphere. The references cited below describe the details of our research in more depth. In addition to the publications listed below we have described the results of our research at NASA AEAP and AGU Fall meetings.

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Improved Solar Atlas from ATLAS-3 ATMOS Spectra

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Research Objectives

The solar absorption technique is commonly used for atmospheric remote sensing of the composition of the Earth's atmosphere. The ATMOS instrument has flown on four shuttle missions, there are several balloon-borne FTIR spectrometers (e.g., the JPL MkIV interferometer), plus over a dozen ground-based FTIR spectrometers worldwide which employ the solar absorption technique. The fact that the sun is so bright and stable in the infrared makes it possible to obtain high quality atmospheric spectra by using the sun as a source. Unfortunately, the solar spectrum is not a simple Planck function. It contains absorption and emission features arising from gases in the solar photosphere. Although these features are of great interest to astrophysicists, they greatly complicate the analysis of atmospheric spectra, especially in spectral intervals where the atmospheric absorption features of interest are blended with solar absorption lines, because the forward model must then simulate the solar atmosphere in addition to that of the Earth.

An approach that has been successfully employed by the ATMOS team is to ratio the atmospheric limb spectra by a solar spectrum measured high above the Earth's atmosphere. The resulting atmospheric transmittance spectra are free from solar (and instrumental) artifacts. Unfortunately, only instruments which have measured solar spectra from high above the Earth's atmosphere (i.e., ATMOS) can easily exploit this ratioing technique. For balloon and ground-based solar absorption spectrometers the removal of solar absorption features is a major challenge in the analysis of certain spectral regions.

The objective of this task is to facilitate the use of ATMOS exo-atmospheric spectra for the purpose of analyzing solar absorption spectra (both balloon and ground-based). Specifically, we will develop a comprehensive solar linelist covering the 600 to 5650 cm⁻¹ spectral region from which a solar spectrum can be easily generated on an arbitrary spectral grid and resolution.

Summary of Progress and Results

The solar absorption spectra measured by the ATMOS instrument during the 10-day ATLAS-3 mission (October-November 1994) are of much higher quality than those obtained in any of the

earlier missions, due to the much longer integration times that were available for solar viewing. Although these spectra have been made available on the ATMOS homepage, many researchers are still unaware of their existence and continue to use the ATMOS Spacelab-3 exo-atmospheric spectra, which were widely publicized by the 3 volume atlas (NASA RP-1224). There are currently three main impediments to the more widespread use of the ATLAS-3 spectra: (1) The wavelength range is divided into 4 filters, each having slightly different frequency grids, and spectral resolutions. Potential users don't want to have to figure out which ATMOS exo-atmospheric spectrum they should be using for a particular spectral region, nor what its spectral resolution and point spacing are. (2) The ATMOS spectral resolution (0.014 cm^{-1}) is considerably poorer than most of the balloon-borne and ground-based FTIRs which might benefit from the exo-atmospheric spectra. This means that the solar features that are narrower than 0.014 cm^{-1} , such as the OH lines around $700\text{-}1000\text{ cm}^{-1}$, are not fully resolved in the ATMOS spectrum and will therefore not fully cancel when a spectrum of higher resolution than 0.014 cm^{-1} is ratioed by an ATMOS spectrum. (3) The currently available ATMOS solar spectra will, in general, be on a different spectral grid to the atmospheric spectra under analysis and will therefore need to be resampled before being used for the purpose of ratioing the atmospheric spectrum.

To overcome these impediments to the use of the ATMOS exo-atmospheric spectra, we have built upon two pieces of unpublished work that have recently been performed at JPL: (1) Dr. Murray Geller has already performed an accurate frequency calibration of the ATMOS ATLAS-3 exo-atmospheric average spectra from the various filters, and has derived a much improved (with respect to NASA RP-1224) linelist of solar features containing over 16,000 lines. (2) The MkIV team has developed a piece of software for iteratively adjusting a linelist in order to improve the match between a calculation and a measured spectrum. This software has been used previously to fit pseudo-linellists to laboratory spectra of pure gases. However, for this project we have used it to refine the list of solar features, already generated by Dr. Geller, by simultaneously fitting all the ATMOS exo-atmospheric spectra from the various filters, plus a few MkIV high-sun balloon spectra. The MkIV spectra are included not because they are better than the ATMOS spectra (the presence of gas above the balloon makes the MkIV spectra worse than the ATMOS spectra for determining the solar spectrum). The MkIV spectra are still important, however, because of their higher spectral resolution (0.006 cm^{-1}), and because they extend to higher frequencies (5650 cm^{-1}) than the ATMOS spectra (4800 cm^{-1}).

We are currently in the process of iteratively adjusting the solar linelist to better fit the ATMOS and MkIV spectra. When this iterative process has converged, the result will be a linelist from which an infinite resolution solar spectrum can be generated at arbitrary point spacing and spectral resolution. When this work is completed, we plan to place the resulting linelist, forward model, and spectrum on the ATMOS home page, together with a description of how it was developed.

Publications

None

Theoretical Investigation of Clouds and Aerosols in the Stratosphere and Upper Troposphere

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Research Objectives

Clouds and aerosols are important components of the chemical system in the stratosphere and upper troposphere. These particulates provide surfaces upon which heterogeneous reactions occur. Also the condensation and subsequent sedimentation of H₂O, as well as of condensable vapors such as HNO₃ and H₂SO₄, alter the vapor phase chemistry in the stratosphere and upper troposphere. We expand our previous studies of these clouds and aerosols. Our overall goal is to develop predictive models for these aerosols and clouds so that their impact on global chemistry can be better determined. Our first specific goal is to model simultaneously the nitric acid aerosols and water ice clouds that form as air parcels move about the polar vortex. The outstanding research problem in this area is to understand how solid particles form. We use lidar data from AASE to constrain model simulations of the clouds. This study will aid in understanding the different processes that occur in dehumidifying and denitrifying the polar stratosphere and in establishing the mean surface area available for chemical reactions. A second goal is to understand the origins of particles in the tropical upper troposphere, and their sensitivity to environmental conditions. Recent observations show that new particles form in the upper troposphere. We simulate this nucleation and investigate the conditions that favor it. One of our goals is to understand whether nucleation of new particles occurs in the lower stratosphere or not. This work may be relevant to the issue of aircraft exhaust effects in the stratosphere. In addition sub-visible cirrus clouds are common near the tropical tropopause. These clouds may impact the number of small aerosols that enter the stratosphere, and they may impact the water vapor budget of the stratosphere. We are investigating these issues. Finally, we are extending our recent work on volcanic aerosol modeling. We have conducted three-dimensional simulations of the transport of Pinatubo material and one-dimensional models of the microphysical evolution of the Pinatubo volcanic clouds. We plan to unite these efforts by performing microphysical simulations in two and three dimensions. We will consider problems relevant to both the perturbed and ambient stratospheric aerosol layer.

Summary of Progress and Results

We have made considerable progress on the work we proposed to carry out. We have completed a number of studies of the properties of stratospheric particles. Our approach has been to use observations to constrain theories of the freezing of various types of particles and to improve our understanding of their physical chemistry. We have found that the majority of polar stratospheric clouds contain solid, or mixtures of solid and liquid particles. Hence, current concepts that liquid solutions dominate may be inaccurate. We have a study underway to understand how new particles form in the upper troposphere. To date we have been able to reproduce the conditions that are favorable to new particle formation. However, we have not been able to duplicate data on the relations between pre-existing aerosol surface area and the number of new particles formed by nucleation. We are exploring various ideas, such as the importance of different types of nucleation occurring than now expected, to explain these observations. We have conducted a number of studies of sub-visible cirrus and their impact on water vapor in the upper troposphere. In particular we find that air moving into the stratosphere can be supersaturated, calling into question the use of tropopause temperatures to correlate directly with stratospheric water. We also find that in some conditions cloud formation can lead to dehumidification of upper tropospheric air and loss of ice nuclei from the air parcels. We have also been very active in multi-dimensional modeling of the stratospheric aerosol. Using a two-dimensional model, we have shown that downward air flow during the polar night can lead to the formation of new particles at high altitude as SO₂ photolyses and nucleation occurs. This work amplifies earlier one-dimensional studies. We are also in the midst of constructing a three dimensional model of stratospheric aerosols that should add realism to simulations of the aerosol layer.

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Stratospheric Aerosol Microphysics and Physical Chemistry

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Research Objectives

The objectives of this project are to investigate the formation and properties of stratospheric aerosols, including polar stratospheric clouds (PSCs). We have focused on the development of models describing the microphysics of fine particles in the upper atmosphere, and on the interpretation of measurements and laboratory experiments using these models. We have also sought to assess the impact of specific microphysical processes on the composition of the stratosphere and possible connections between aerosol and cloud properties.

Summary of Research Progress and Results

Model Development and Data Analysis: PSC Trajectory Model: We are continuing to refine a trajectory microphysics code originally developed by Drdla [1996] [also, Drdla *et al.*, 1993, 1994]. The primary focus of this work is on the interpretation of aircraft data collected in a series of polar stratosphere field experiments. We are correlating measurements taken at the aircraft with simulations carried out along air parcel trajectories terminating at the same points. The model has been modified to include a detailed treatment of ternary solution aerosols, which evolve into type-1b PSCs [Tabazadeh *et al.*, 1994a], as well as surface chemical processes [Tabazadeh and Turco, 1993]. Previous applications of the trajectory model had identified the dominance of type-1b aerosols in a number of the aircraft observations [Drdla *et al.*, 1994; Tabazadeh *et al.*, 1994b]. In a series of papers currently in preparation [Drdla *et al.*, 1999], the aircraft data are further analyzed to identify phase changes that may be occurring within the PSCs, especially transitions between type-1a and type-1b clouds. Also of interest is the determination of the solid phases that may be present, including nitric acid trihydrate (NAT), dihydrate (NAD), and monohydrate (NAM), as well as possible amorphous ices, sulfuric acid tetrahydrate (SAT), and other compounds. In the model, a small subset of the physical/chemical parameters (e.g., freezing point supersaturations over the liquid phase) are varied to optimize the agreement between simulations and observations. A consistent problem that arises in these studies is quantifying the freezing properties of the liquid aerosols, and predicting the onset of nucleation of water ice. Nevertheless, the outcome of numerous sensitivity studies indicate that there is a small sub-class of liquid aerosols that are prone to freeze upon supercooling, and that particles these control dehydration and denitrification of the lower stratosphere.

Satellite PSC Analysis: To analyze PSC phase changes in greater detail, additional information is required along air parcel trajectories. Accordingly, we developed a unique approach to study

PSC evolution using extensive multispectral solar extinction measurements derived from the SAM (Stratospheric Aerosol Measurement)-like POAM (Polar Ozone and Aerosol Measurement) satellite system [Steele *et al.*, 1999]. Leading up to this analysis, we had investigated the characteristics of limb-extinction aerosol/ozone observing systems, concentrating on SAGE retrievals of basic aerosol physical properties [Steele, 1998; Steele and Turco, 1997a, b]. In that work, it was shown that Stratospheric Aerosol and Gas Experiment (SAGE) observations are capable of yielding integrated aerosol properties with reasonable accuracy; in particular, the total surface area density and particle mass may be obtained, typically, within 20 percent). Importantly, we also identified and corrected an error in the standard SAGE ozone retrieval algorithm [Steele and Turco, 1997a], which subsequently led the SAGE team to recalibrate their data archive.

Turning to POAM in more recent collaborative work, we designed a robust inversion algorithm for the POAM sensor [Steele *et al.*, 1998]. Since POAM collects extinction data at several wavelengths, and probes the polar winter stratosphere essentially along circumpolar trajectories, these data may be used to identify changes in the aerosol size distribution (based on changes in the measured extinction spectra), and to associate such changes with variations in meteorological conditions along streamlines. The trajectory model described earlier has also been run along the same trajectories, and PSC predictions (converted to the equivalent extinction) contrasted with observations [Steele *et al.*, 1999]. Along certain trajectories, the model is able to reproduce sequences of phase (size distribution) transitions. However, in some instances the predicted phase change at a particular stage of cloud evolution is not consistent with satellite data; sensitivity tests suggest that the treatment of aerosol freezing is inadequate.

Analytical Aerosol Model: We have derived a new analytical solution for the evolution of the aerosol size distribution in an air parcel undergoing, simultaneously, mixing, coagulation, and condensation [Turco and Yu, 1999a]. The solutions are quite general and apply to a number of common situations, such as aircraft plumes, volcanic clouds, and smokestack plumes. Initially, we derived a simple relation for the total population of aerosols subject to coagulation in an expanding plume [Turco and Yu, 1997]. That solution revealed that the number of particles eventually dispersed into the global atmosphere is independent of the number initially emitted, and depends instead only on the mean coagulation kernel and the rate of plume expansion. We defined a new dimensionless number that depends on these parameters and is equivalent to the asymptotic total number of particles [Turco and Yu, 1997]. We next derived a simple analytical solution for the particle size distribution in an expanding, coagulating plume as a function of time [Turco and Yu, 1998]. Most recently, we have extended these analytical size distributions to include the effects of condensation of primary and secondary vapors, and the effects of background aerosols [Turco and Yu, 1999a].

Our analytical size distributions can be used to estimate more accurately useful aerosol parameters such as the surface area density, heterogeneous reactivity, and optical extinction [Turco and Yu, 1998], and may also be employed to analyze field data and to validate complex numerical microphysics codes. Further, such relations can be used to initialize two- and three-dimensional models, where it would otherwise be difficult to determine the aerosol properties at the time a plume has expanded to the scale of the resolution of the model [Turco and Yu, 1998, 1999a]. Our analysis of aircraft plumes using the analytical results suggests that very large populations of nucleated particles are unlikely to survive coagulation under typical conditions

encountered in the atmosphere, limiting the concentrations of new particles that are likely to be injected by high-flying aircraft [Turco and Yu, 1997, 1999a].

Aerosol Formation Studies: Condensation on Chemiions—During the course of this project, we investigated the role of ionization in the formation and properties of aerosols in the lower stratosphere and troposphere. Initially, this work was carried out in the context of the production of new sulfate aerosols in aircraft plumes. We introduced the idea that chemiionization generated in aircraft engine combustors is responsible for the evolution of the volatile aerosols observed in high-altitude plumes, owing to electrostatic influences on the microphysics of ultrafine particles [Yu, 1999; Yu and Turco, 1997, 1998a, b]. This suggestion followed our earlier identification of homogeneous binary nucleation of primary sulfuric acid and water vapors emitted by the engines as the likely source of volatile particles seen in atmospheric plumes [Zhao and Turco, 1995]—as opposed to the emission of sulfur dioxide, with subsequent oxidation in air to form sulfuric acid followed by homogeneous nucleation. More recent field data were inconsistent with the homogeneous nucleation theory, however. Our introduction of “charged” microphysics has now led to a reconciliation of numerical plume simulations with a variety of field observations [Yu and Turco, 1997, 1998a, b; Yu *et al.*, 1998; Kärcher *et al.*, 1998].

Further analysis using the chemiion model has revealed the important contribution of organic fumes from combustors in generating volatile ultrafine particles upon chemiions in cases where fuel sulfur content is reduced drastically [Yu *et al.*, 1999]. We recently extended the plume microphysical simulations to quantify the number of plume aerosols that might survive and eventually grow into cloud condensation nuclei (CCN) [Yu and Turco, 1999a]. The results show that, depending on the time of year and corresponding ambient environmental conditions, a substantial number of chemiion-mode aerosols can evolve into CCN, but that the number is strongly limited by the physics in the early plume—namely the restricted number of chemiions (owing to charge recombination) and subsequent coagulation [Turco and Yu, 1998].

Nucleation by Ion-ion Recombination—The presence of ions throughout the atmosphere has been known for many years, but the linkages between atmospheric charge and conductivity, aerosol formation and evolution, cloud microphysics, and atmospheric chemistry have remained undefined. Under this project, we have investigated the properties of aerosols in the upper troposphere and lower stratosphere, with the goal of defining the dominant formation processes. We had earlier quantified the role of homogeneous nucleation in forming new particles in this region. We have now identified a new, potentially dominant *in situ* source of volatile aerosols [Turco *et al.*, 1998, 1999]. The process is connected with the natural ions formed throughout the lower atmosphere by penetrating galactic cosmic rays. These ions can achieve massive sizes by rapid and efficient molecular clustering; upon recombination, the largest of these ions may generate stable neutral embryos. Nucleation by ion-ion recombination (NIIR) explains a variety of observations indicating a slow, steady supply of aerosols in relatively clean air. The theory also directly links emissions of aerosol precursors, such as dimethylsulfide (DMS) from oceans, as well as organic compounds from vegetation, with the formation and growth of aerosols, some of which eventually grow into cloud condensation nuclei. NIIR may, therefore, provide a long-sought quantitative link between DMS emissions and cloud microphysical/radiative properties. We have roughly calibrated the rate of NIIR using observed ultrafine particle measurements, and

interpreted aerosol behavior in the boundary layer by employing this mechanism in a detailed microphysics model [Turco *et al.*, 1998].

We are currently investigating the thermodynamics of charged atmospheric clusters of very large size, using laboratory data for relatively small clusters and the Thomson phenomenological model at large cluster sizes. This quantification of the mass distribution of large ions will be used to extend our theory of stable particle formation by ion-ion recombination. Simulations of aerosol evolution following NIIR are being carried out in the context of field observations of ultrafine aerosol properties, focusing on the Aerosol Characterization Experiment (ACE) missions [Turco and Yu, 1999b].

Polar Stratospheric Ions—We are considering the role of large nitrate cluster ions in the production and phase changes of PSCs at extremely low temperatures [Turco and Hamill, 1999]. This work is closely related to the research on nucleation (NIIR) described above. It is well known that background ionization associated with galactic cosmic rays leads to the formation of large nitric acid cluster ions in the lower stratosphere. These polar stratospheric ions (PSI) might be the precursors of new PSC particles. Further, the largest PSI might act as ice contact nucleation embryos at low enough temperatures, leading to the formation of type-1a PSCs (frozen nitric acid ices).

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C. GLOBAL CHEMICAL MODELING



Modeling of Isotope Fractionation in Stratospheric CO₂, N₂O, CH₄, and O₃: Investigations of Stratospheric Chemistry and Transport, Stratosphere-Troposphere Exchange, and Their Influence on Global Isotope Budgets

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Research Objectives

Until recently, the stable isotopic composition of chemically and radiatively important stratospheric species, such as O₃, CO₂, N₂O, and CH₄, was largely unexplored, despite indications from the few measurements available and theoretical studies that global-scale isotopic variations will provide a unique tool for quantifying rates of global-scale mass transport into, within, and out of the stratosphere and for understanding the mechanisms of chemical reactions involved in ozone production. The number and geographical extent of observations are beginning to increase rapidly, however, as access to the stratosphere, both directly and by remote-sensing, has increased over the last 5 years and as new analytical techniques have been developed that make global-scale isotope measurements by whole-air sampling more feasible. The objective of this study, begun in April 1999, is to incorporate into the Livermore 2-D and 3-D models the likely photochemical fractionation processes that determine the isotopic compositions of stratospheric CO₂, N₂O, CH₄, and O₃, and to use the model results and new observations from NASA field campaigns in 1996 and 1997 to investigate stratospheric chemistry and mass transport. Additionally, since isotopic signatures from the stratosphere are transferred to the troposphere by downward transport at middle and high latitudes, the isotopic compositions may also serve as sensitive tracers of stratosphere-to-troposphere transport. Comparisons of model results with stratospheric and upper tropospheric observations from these campaigns, as well as with ground-based observations from new NOAA and NSF-sponsored studies, will help determine whether the magnitudes of the stratospheric fractionation processes are large enough to use as global-scale tracers of transport into the troposphere and, if so, will be used to help constrain the degree of coupling between the troposphere and the stratosphere. Moreover, while isotopic studies in the troposphere have already provided a wealth of information on the natural and anthropogenic sources and sinks of CO₂, CH₄, and N₂O, the

influence of stratospheric fractionation processes on the tropospheric isotopic compositions has received only scant attention, despite evidence that it may be quantitatively important. The ability to model global-scale variations in the isotopic compositions of stratospheric species and their transfer to the troposphere will help distinguish between fractionation occurring in the atmosphere and that which results from biological or industrial processes, in principle allowing more accurate global budgets for CO₂, N₂O, and CH₄ to be derived if the influence of the stratosphere is determined to be significant.

Summary of Progress and Results

The Livermore 2-D model (LOTUS) has been set up and is now successfully running at UC Berkeley. Isotope-specific chemistry has been incorporated for CH₄, the species with the most well-characterized and simplest fractionation mechanism and kinetics. In short, CH₄ becomes enriched in ¹³C as CH₄ mixing ratios decrease since the ¹²C isotopomer reacts more rapidly with Cl and OH than does the ¹³C isotopomer (by 7 percent and 5 per mil, respectively, at stratospheric temperatures). A preliminary comparison of the 2-D model results with the most extensive set of observations so far available for stratospheric $\delta^{13}\text{CH}_4$ [Sugawara *et al.*, GRL, 1997], along with initial sensitivity studies, show that the temperature-dependent rate coefficients are well characterized by laboratory experiments: large deviations in the $\delta^{13}\text{CH}_4:\text{CH}_4$ relationship between the model and observations occur when relatively small changes in the rate coefficients are implemented in the model (changes which are in many cases much larger than overall expected changes in the relationship over the entire stratosphere). In addition, the model results predict that much larger fractionations will be observable in air descending in the polar vortices (such as air sampled during the POLARIS and the upcoming SOLVE field missions) than were observable from the balloon platform of Sugawara at midlatitudes. Sensitivities to model transport will be investigated next, as will incorporation of the isotopic composition of the products of methane oxidation (Motivation for the latter stems from several measurements of $\delta^{13}\text{CO}$ in the Southern Hemisphere lowermost stratosphere by Brenninkmeijer *et al.*, JGR, 1995]). Model runs are also underway to estimate the steady-state contribution of heavy CH₄ to the overall isotopic composition of CH₄ in the free troposphere; while the stratospheric contribution is expected to be relatively small, even small influences from the stratosphere could alter interpretations of the 1 per mil interhemispheric gradient in $\delta^{13}\text{CH}_4$ with respect to methane surface fluxes, for example. After characterization of the CH₄ system, isotope-specific chemistry for O₃, CO₂, and N₂O will be incorporated, tested, and model results interpreted and compared against observations.

Publications

None

Three-Dimensional Model with Interactive Biosphere

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Summary of Progress and Results

The MOZART model is a three-dimensional chemical-transport model that extends from the surface to approximately 35 km altitude, and provides the global distribution of 50 chemical compounds including ozone and most of its precursors (nitrogen oxides, carbon monoxide, methane and seven other primary hydrocarbons). Fast-reacting radicals (e.g., OH, HO₂), peroxides (H₂O₂, CHOOH, C₂H₅OOH), as well as intermediate VOCs (aldehydes, acetone, etc.) are also included in the chemical scheme.

The distribution of these species is obtained by solving approximately 50 coupled continuity equations with appropriate initial and boundary conditions. These equations account for surface emissions and dry deposition, boundary layer exchanges, long-range (resolved) transport, (parameterized) convective transport, chemical and photochemical conversions (gas-phase and a limited number of heterogeneous reactions), and wet scavenging. The equations are solved on a numerical grid with a 2.8° × 2.8° (latitude, longitude) resolution and usually 33 levels in the vertical.

The first version of the model (MOZART-1) is described by Brasseur *et al.* [1998] and evaluated through detailed comparisons with available observations by Hauglustaine *et al.* [1998]. MOZART-1 has been used to address a number of scientific issues including (1) the role of lightning in the formation of upper tropospheric ozone in the Southern Hemisphere [Hauglustaine *et al.*, 2000], and (2) the impact of extensive fires in Indonesia during the last El Niño event [Hauglustaine *et al.*, 1999]. Other runs have been made to assess (1) the changes that have occurred since pre-industrial times in the chemical composition of the troposphere, and (2) the response of the troposphere to the current fleet of subsonic aircraft. Model integrations simulating the future evolution of the atmospheric composition, based on IPCC scenarios, have also been completed and will soon be published.

A second version of the model (MOZART-2) has recently been completed. This version includes several improvements over MOZART-1 among which is the implementation of the Lin and Rood transport scheme (which replaces the nonconservative semi-Lagrangian transport scheme of Williamson and Rasch). In addition, the model can now be run using analyzed dynamical fields rather than meteorological information provided by the NCAR Community

Climate Model (CCM). Surface emissions of anthropogenic and biogenic compounds have also been updated.

A third version of the model (MOZART-3) is currently being developed. This model is similar to MOZART-2, but extends to 80 km (rather than 35 km) and includes 90 chemical species to account not only for tropospheric processes, but also for stratospheric and mesospheric reactions (including heterogeneous chemistry).

Finally, much effort has been devoted to represent “on line” exchanges of chemical compounds between the ecosystems and the atmosphere. The BACH (Biosphere and Atmospheric Chemistry) module coupled to MOZART is a “flux coupler” that accounts for surface emissions/deposition over different types of terrestrial ecosystems or over the ocean.

MOZART has been used to analyze observations from field campaigns (e.g., MLOPEX II), plan new field experiments (TOPSE), address scientific questions (processes responsible for ozone production/loss in the tropics), and to participate in international assessments (new IPCC assessment). A study to quantify the role of heterogeneous and aqueous phase chemistry is currently underway. Updated formulations for the emissions of isoprene and several other nonmethane hydrocarbons, based on the new model of Alex Guenther at NCAR are also being introduced.

Finally, an elaborate database including a large number of existing observations, developed and maintained by L. Emmons at NCAR, is used to constantly validate MOZART. The model has also been made available to several universities and research groups in the country and abroad.

Publications

None

Impact of Mineral Aerosols and Asian Emissions on the Chemistry of the Troposphere

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Research Objectives

The transport and chemical characteristics of the regional trace gas cycles in east Asia with specific emphasis on ozone and mineral aerosols is the focus of our current NASA grant. This project uses three-dimensional simulations of the transport and chemical processes to investigate tropospheric trace gas cycles in east Asia and to explore the possible interactions between dust and tropospheric chemistry. The primary goals of this research are to further identify and quantify the role of mineral aerosol as a reactive surface in the troposphere, and to examine the impact of regional emissions from east Asia on the Northern Hemisphere.

Summary of Progress and Results

Research on this project has focused on: (1) regional simulations of ozone and aerosol interactions in east Asia; (2) improved estimates of NO_x emissions for Asia and an evaluation of the growth in Asian emissions on tropospheric ozone; (3) extension of modeling analysis to include explicit treatment of aerosol composition; and (4) the application of these procedures to study these interactions of Asian emissions on regional and global scales, with an emphasis on the Pacific Rim region. An important aspect of the regional scale modeling is the characterization of the anthropogenic emissions. One critical aspect of modeling in Asia is the necessity to take into account the dynamic nature of emissions. As part of this project we have used a detailed data base on energy in Asia to estimate NO_x emissions in the future based on energy pathways and mixes of control technologies. We estimate NO_x emissions for China in 1990 to be 8.2 Tg-NO₂/yr, growing to 13.8 Tg-NO₂/yr in 2000 and 32.3 Tg-NO₂/yr in the year 2020. These estimates are region specific and yield 1° × 1° gridded emissions for both area and elevated sources. These results point out the fact that major changes in the atmospheric environment in this region can be expected over the next 10 to 20 years.

These emissions have been used to investigate ozone production on regional and global scales using three-dimensional models. At the regional scale the photochemical production of ozone was found to be important in the regions over the precursor source regions, and in the continental outflow zones. Calculated production efficiencies for ozone were found to be similar to those

observed and calculated over North America. The regions of strong photochemistry were largely restricted to the lowest 3 km of the atmosphere. However in regions of convective activity the chemical production zones reach the mid troposphere. These results indicate that ozone in the lower troposphere in this region can be strongly influenced by both continental outflow of precursors and by the downward transport of ozone-rich air which occurs frequently in conjunction with strong continental outflow episodes. Simulations were performed at the global scale using 1990 emissions and then again using 2020 Asian emissions and 1990 emissions for the rest of the world. The growth in Asian NO_x emissions was found to result in an increase of 20 to 50 ppb throughout Asia and the western Pacific, and an increase in between 10 to 20 ppb throughout the mid-latitudes of the entire Pacific Ocean area.

Research has also focused on the interaction between mineral aerosols and the photochemical oxidant cycle in Asia. Specific studies include: (1) the modeling of dust transport in east Asia and the interactions of the trace gas species with mineral aerosols for the period of May 1987; (2) simulation of smoke associated with a forest fire episode in Northern China for the month of May 1987; (3) box model simulations to better understand aerosol-chemistry interactions including partitioning of nitric acid and direct ozone reactions and renoxification reactions on aerosol surfaces; and (4) analysis of the NMHC transport and chemistry in east Asia during a spring continental outflow period. These studies have made extensive use of aerosol-TOMS products. Results from these studies have shown that chemical interactions with mineral dust particles may increase the SO₂ to sulfate conversion rates and cause an increase in the partitioning of nitric acid to the particulate phase. These effects may have significant impacts on local and regional trace gas cycles.

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Intercontinental Assimilation Modeling of C and N Chemistry Affecting Tropospheric Ozone

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Research Objectives

This program used three-dimensional computer models whose results were closely compared to data analysis of individual weather events during special aircraft observing missions. It was deployed to reveal mechanisms of very long-distance transport of pollutants in the upper atmosphere below the main ozone layer (this region is known as the upper troposphere). In one set of missions, it was necessary to trace pollution nearly around the world, from South America to Tahiti. Secondly, it was used to make quantitative checks on the way that assessment models capture the effects of thunderstorm clouds as they loft pollutants and other trace species to allow this intermittent but global spread. Study objectives moved from general descriptions of intercontinental tropical smog to the budget-checking of the sources of carbon monoxide and reactive nitrogen oxides; these compounds control the ozone and reactive radicals which accompany the smog. These results are useful in understanding the degree of chemical perturbation of the global temperature balance and ultraviolet shield by resulting from large pollutant sources as agricultural burning and aircraft emissions, which seem greater than expected, and comparing them to natural effects, e.g., of lightning.

Summary of Progress and Results

Initial work studied the effects of biomass burning emissions of South America and Africa as they affect a huge region centered on the Equatorial Atlantic. These studies showed that Africa was the predominant source of pollution that creates a very large and visible buildup of tropospheric ozone over the Equatorial Atlantic in the Southern-Hemisphere springtime. This ozone is visible in when the satellite-borne Total Ozone Mapping Spectrometer is analyzed to remove the large contribution of stratospheric ozone (J. Fishman, NASA Langley Research Center). Pollution comes from burning in the tropics, partially from deforestation but more from burning associated with agriculture and pastures. Carbon monoxide, a variety of hydrocarbons, nitrogen oxides, and pollution ozone are lofted above a clean oceanic atmosphere layer to influence the huge area between the Congo and Amazon forests, and to the south. Our

simulations of the smog cycle during transport suggested that most Central Atlantic ozone was formed within a few days of the source and then transported.

The meteorology of lofting was novel and important. We found that lofting included thunderstorm venting but also non-cloud mixing which reached a surprising 4-5 km above the surface; this mixing pattern and the thunderstorms were married in a complex convergence-divergence pattern along the Inter-African Front. Large sources of carbon monoxide, CO, (observed by the Glenn Sachse group, NASA Langley Research Center) must be emitted from the tropical land surface to match the DC-8 aircraft observations above Southern Africa and far off the coast; our simulations showed this by quantifying the outflow in large-scale wind patterns. A later study confirmed these patterns and additionally demonstrated that the vertical distribution of carbon monoxide provides an excellent and much-needed test of vertical transport effectiveness in global-scale models. Our meteorological mechanisms were also able to describe the general features of CO observed by another satellite instrument, the shuttle-borne Measurement of Atmospheric Pollution (MAPS). Besides the aircraft measurement program, TRACE-A (Tropical Atmospheric Chemistry near the Equator – Atlantic), a field program, the Southern Africa Fire Atmosphere Research Initiative (SAFARI), involved ecologists in the measurement of the burning of plant carbon to make CO. Major questions remain: our simulation, and many others that have followed, require 3 to 10 times more CO than the ecologists can produce from their estimates of the fuel that is burned. This is may be called the “missing carbon source.” There is also a “missing nitrogen sink,” since our model suggested that reactive nitrogen oxides should be transformed into less-reactive forms like nitric acid or peroxyacetyl nitrate. These are not observed in appropriate quantities. The aircraft observations and our simulations provide no clear view of this “missing nitrogen sink.” Perhaps nitrogen removal to smoke or dust is involved.

Simulations and comparisons then moved to the global atmosphere. When a later aircraft mission reached Tahiti and other points in the remote South Pacific in the PEM-Tropics B intermittent observations of strong pollution, we were able to explain this in terms of transport from Africa and especially South America, in a “Southern Global Plume.”

In addition to the transport of smog ozone from polluted continents, measurements show that ozone continues to be made in the upper troposphere, but the details of the smog precursor patterns are not completely clear. We had described fifteen years ago how cloud-vented hydrogen peroxide and other “radical precursors” greatly energize ozone production in the upper atmosphere from 5 to 15 km (below the ozone layer). The effects of these radicals and their interaction with reactive nitrogen oxides (also necessary for smog) are complex. The large role of acetone compared to peroxide compounds in the production of ozone was the topic of one paper published in the course of this research. Another paper submitted for publication describes how acetone and nitrogen oxides tend to nullify each others contribution to ozone production, and how this effect tends to disappear when nitrogen oxides are put into the atmosphere at high concentrations. This research proved very helpful in assessing the complex roles of lightning and aircraft on global tropospheric ozone.

Techniques of computer simulation and close analysis of observations that were developed in this research period proved extremely useful in recent work on the effects of aircraft and lightning in controlling ozone production over the North Atlantic, the Subsonic Assessment Program Ozone and Nitrogen Oxide Experiment (SONEX), taking place in the autumn of 1997.

We have found that (a) Aircraft emissions provided 35–60% of the active nitrogen oxides over the North Atlantic during this period; (b) Lightning provided even more NO_x than aircraft emissions at the main oceanic flight altitudes (~10–11.5 km), but very rarely had strong effects below ~10 km! (c) Contrary to our expectations, urban and industrial pollution effects contributed only moderate amounts of NO_x, and mostly below 8 km, and very intermittently. (d) Stratospheric air influencing the Northern Hemisphere troposphere often depressed NO_x concentrations, and the influence seemed very contingent on the details of stratospheric processes. Possibly this presumably involved transformations that took place on aerosols. Furthermore, some fascinating irregularities in the levels of atmospheric radicals (OH and HO₂) were associated with upper tropospheric processes, (aircraft or lightning sources), not radical-source compounds from the lower troposphere. (We and other scientists had expected that other compounds similar to acetone and hydrogen peroxide, deriving from the near-surface atmosphere, might somehow be responsible.) These irregularities in the simulation of the radicals seem to have important implications. A brief summary of our continuing works is this: when simulations are corrected to include better radical simulation and high contributions of aircraft NO_x, we may expect that the potential role of an increasing aircraft fleet will become of much greater scientific interest.

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Anthropogenic and Natural Contributions to Sulfate Aerosol Over the Oceans: Modeling and Data Analysis Using A 3-D Model Driven by Assimilated Meteorology

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Research Objectives

A 3-year modeling and data analysis program is proposed to study anthropogenic and natural contributions to the sulfate aerosol loading over the Pacific and Atlantic Oceans. Our specific objectives are: (1) to quantify the amount and route of continental outflow for different seasons; (2) to improve our knowledge of DMS chemistry by constraining the DMS emission flux, oxidation rates and pathways in accord with observed atmospheric concentrations of DMS and its oxidation products; and (3) to investigate the relative importance and influence of anthropogenic versus natural sources of sulfate in the marine boundary layer and free troposphere.

Summary of Progress and Results

Our ACMAP project in the past 3 years focused on simulations of sulfate aerosol and its precursors in the Goddard Ozone Chemistry Aerosol Radiation and Transport (GOCART) model and on analysis of sulfur data from various field campaigns. Our major results are summarized below.

(1) *Simulation of Tropospheric Sulfate:* Based on the transport model of Lin and Rood [1996], we have developed the GOCART model for tropospheric sulfate by incorporating sulfur emission, chemistry, Dry deposition, and wet scavenging modules. Four sulfur species are simulated: Dimethylsulfide (DMS), methanesulfonic acid (MSA), SO₂, and sulfate. We have conducted more than 6 years of sulfur simulations (1990 to 1996), covering the periods of NASA GTE aircraft missions of Pacific Exploratory Missions (PEM-West A, PEM West-B, and PEM-Tropics A) and other agency sponsored field programs, such as ACE-1 and ACE-2. The model description, the simulated global distribution of sulfur species and their budget are presented in Chin *et al.* [1999a].

We have evaluated the model extensively with observations from ground-based networks and from several field campaigns of PEM and ACE. Our results shows that the model well captures the observed sulfate and its precursor concentrations, their spatial and temporal variations, and their vertical profiles under various conditions. This is largely due to the realistically assimilated winds and other physical and chemical parameters used in the model.

(2) *Simulation of Rn-222 and Pb-210:* Simulation of Pb-210 was motivated by the necessity of testing model's wet scavenging parameters. Naturally, Rn-222 was also simulated as it is the precursor of Pb-210. Rn-222 can be used as a label for continental airmass in other simulations. We have found an excellent agreement between modeled and observed Rn-222 vertical profiles measured over California and over the North Atlantic, an agreement which indicates that the model transport is realistic. We also found that, compared with observations, the wet deposition scheme, which accounts for the loss of soluble species by rainout and washout as well as within the convective cloud updraft, is reasonably representative of the wet scavenging process.

(3) *Extracting Relevant Fields from the GEOS DAS Data:* The GEOS DAS meteorological fields archived by the Data Assimilation Office are in very large file sizes, with more than 80 prognostic and diagnostic fields saved. Since we need only less than 25 of these fields, we have extracted the desired subsets from the original data set for more efficient file manipulation. We have also calculated the turbulent diffusion coefficients for the 1990-1996 time period, as they were not saved in the earlier GEOS DAS system but are necessary for modeling the turbulent mixing and diffusion processes. These subsets are available for public access.

(4) *Participation in International Model Intercomparison and Assessment:* The GOCART model of sulfate and Rn/Pb was part of the IGAC sponsored Comparison Of Sulfur Atmospheric Models (COSAM). In addition, we have been participating in the IPCC assessment of aerosol radiative forcing activity by providing sulfate and other aerosol concentrations and optical thicknesses using future emission scenarios.

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Global Studies of the Sulfur Cycle Including the Influence of DMS and Fossil Fuel Sulfur on Climate and Climate Change

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Research Objectives

Atmospheric aerosols have significant effects on climate through their impact on the Earth's radiation budget. While a variety of aerosol types exist in the atmosphere, volatile sulfur compounds are particularly important aerosol precursors. Our studies have been focused on developing an understanding of global and regional sulfate aerosol abundances and investigating their direct and indirect climate effects with a fully coupled climate/chemistry model. Our research indicated that anthropogenic emissions of SO₂ are large enough (relative to natural sources) to produce significant increases in sulfate aerosol abundances in the Northern Hemisphere. Our calculations also showed that these anthropogenic sulfate aerosols might decrease the globally averaged solar radiation absorbed by the Earth-atmosphere system through the direct effect by about -0.4 Wm⁻². With different approaches for the formation of anthropogenic sulfate and its relation to aerosol size distribution, the indirect forcing may range from -0.6 to -1.6 Wm⁻². This range reduced to -0.4 to -1.1 Wm⁻² if a prescribed marine background particle number concentration was universally applied over the ocean. These calculations did not include the natural aerosol emissions of dust and sea salt that also serve as cloud condensation nuclei. To better characterize the role of sulfur emissions in climate and climate change, we will extend our coupled model to incorporate all the important aerosol types in the troposphere.

Summary of Progress and Results

We have extended our chemistry model (GRANTOUR) to treat the global-scale transport, transformation, and removal of SO₂, DMS, H₂SO₄, organic carbon and black carbon species in the atmosphere. We included all the relevant sources of sulfur in the troposphere from fossil fuel combustion, industry, biomass burning, ocean, volcanoes, and terrestrial sources. Besides the aforementioned sulfur species, we extended to include black and organic carbon. Anthropogenic black and organic carbon particles are mainly from sources such as biomass burning and fossil fuel combustion, whereas natural organic particles come from photochemical conversion of gaseous emissions from vegetation and from direct emission of particles from plants. We have also completed a dust aerosol modeling capability to investigate the transport and deposition of dust over the open ocean. Dust source regions were identified from the 1° × 1° soil moisture

data as those regions that perennially contain < 15 mm soil water. We have developed an algorithm relating the monthly average surface wind speed to the monthly average dust source strength for two ranges of dust particle radii: 0.1 to 1 μm and 1 to 10 μm . We have not included dust particles with radii > 10 μm because these particles have atmospheric residence times that average only a few hours and are usually not transported long distances from their source regions. Furthermore, a newly developed sea salt emissions inventory has been incorporated into our model to obtain a more accurate representation of aerosol characteristics in the atmosphere. These carbonaceous, dust, and sea salt aerosols will serve as pre-existing background particles on which H_2SO_4 condenses. At each stage of our model extension to new aerosol species, we have taken care to compare with the available relevant data and to gain an understanding of the adequacy of the model.

To estimate the direct climate forcing of anthropogenic sulfate, we have modeled optical properties of sulfate aerosols to account for changes in the refractive indices with relative humidity. We have updated our solar radiation module with a higher spectral resolution to properly capture the variation of aerosol optical properties with wavelength. We have also initiated a study to examine the direct climate forcing corresponding to the temporal variations in regional anthropogenic fossil fuel SO_2 emissions caused by changes in local populations and different activities for the years 1950 through 2010. To estimate the indirect effect, the effect of anthropogenic sulfate on initial cloud drop number concentration was parameterized as a function of aerosol size distribution, total number, and updraft velocity at cloud base. This parameterization is based on a mechanistic description of droplet formation and the chemical processes controlling the formation of sulfate. It accounts for anticipated changes in aerosol size due to changes that result from the deposition of sulfate formed in aqueous reactions and the condensation of sulfate formed in homogeneous gas-phase reactions. We have evaluated this parameterization by comparing the predicted effective droplet size with that retrieved from satellite data and other measured correlations between droplet concentration and aerosol concentration. In contrast to the direct effect that is more significant over the land, the indirect effect is much more pronounced over the ocean where clouds are relatively optically thin and likely to be of higher susceptibility. Our simulations also indicated that anthropogenic sulfate may result in important increases in reflected solar radiation, which would mask locally the warming from increased greenhouse gases.

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3-D Chemistry and Transport Model

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Research Objectives

The objective of this research is to identify and quantify photochemical and transport mechanisms that control stratospheric ozone, in order to improve the capability to predict future ozone response to natural and man-induced changes in stratospheric composition and climate. The GSFC 3-D Chemistry and Transport Model (CTM) was developed as the primary tool to achieve this objective. This model uses winds and temperatures from the NASA Goddard Earth Observing System Data Assimilation System and a complete representation of stratospheric photochemistry to calculate the evolution of ozone and other trace species. Results of simulations are compared with observations from a variety of platforms – aircraft, sonde, balloon, ground-based and satellite - with the goal of identifying and clarifying the transport and photochemical processes that contribute to the observed constituent behavior.

Summary of Progress and Results

The 3-D CTM uses winds and temperatures from the Goddard Earth Observing System Data Assimilation System and a complete representation of stratospheric photochemistry to calculate the evolution of ozone and other trace species. The results of these simulations have been used to explain constituent behavior as observed by aircraft, satellite, balloon, and ozonesonde. Simulations are compared directly with observations, and focussed physical and chemical processes. Douglass *et al.* [1997] compared modeled ozone evolution in the middle latitude middle stratosphere with observations of ozone and long lived trace gases from the Cryogenic Limb Array Etalon Spectrometer (CLAES), the Microwave Limb Sounder (MLS) and the Halogen Occultation Experiment (HALOE), all on the Upper Atmosphere Research Satellite (UARS) to show that the interplay between transport by planetary waves and photochemical destruction of ozone was well represented in the model. Douglass and Kawa [1999] used the model to account for transport effects and observations from HALOE, CLAES and MLS to clarify the dependence of the springtime formation of chlorine reservoirs on the ozone concentration and temperature in the high latitude lower stratosphere. This model was used to identify important transport mechanisms in the lower stratosphere. Rood *et al.* [1997] showed that troposphere to stratosphere exchange could take place between the upper tropical

troposphere and middle latitudes associated with storms. Recently, Rood *et al.* [1999] used HALOE ozone observations and ozonesonde data to show that the annual cycle of ozone changes phase between the lowermost stratosphere and the 400K potential temperature surface, which is a result of seasonal changes in the transport mechanisms which contribute to the ozone distribution. This change is also evident in the model field.

The model simulations were evaluated using diagnostics of atmospheric transport based on observations. Strahan *et al.* [1998] used ER-2 observations of CO₂ to diagnose pathways of transport in the lower stratosphere. Weaver *et al.* [1999] compared laminae produced by a high vertical resolution version of the model with a climatology derived from ozonesonde profiles, and found that the model production of lamina was realistic at high latitudes but excessive in the tropics. This analysis also showed that the ozone budgets produced from the high resolution run and from the base run were similar. Generalized diagnostics were developed which could be applied to simulations made with winds from a general circulation model as well as to simulations using assimilation, and used to evaluate the wind fields to be used in assessment as part of the Global Modeling Initiative [Douglass *et al.*, 1999].

This CTM was used in support of the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission, and run in near real time to provide global context for the aircraft observations. The latitude dependence of ozone loss and its partitioning among hydrogen, nitrogen and halogen radicals derived from the POLARIS observations agrees well with the modeled ozone loss at ER-2 altitudes.

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Two-Dimensional Modeling Studies of the Middle Atmosphere

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Research Objectives

To study the processes that control photochemistry, radiative transfer and transport in the middle atmosphere. Topics examined include the effect of interannual variations in aerosol concentration (due to major volcanic eruptions) on the long-term trend of ozone depletion; the effect of heterogeneous chemistry in the near-tropopause region on ozone; and an examination of the heat budget of the stratosphere using observations and model calculations.

Summary of Progress and Results

- The GS model has been used to study various aspects of aerosol chemistry in the middle atmosphere. The work has centered on the evaluation of the role of interannual aerosol variations on ozone trends. The importance of taking into account these ozone variations is demonstrated in connection with the 1991 Mt. Pinatubo eruption [Solomon *et al.*, 1997].
- The model has also been used to investigate the importance of heterogeneous chemistry in the near tropopause region. It has been shown that ClONO₂ can react with HCl and with H₂O on subvisible cloud particles in the lowermost stratosphere to produce active chlorine. Significant ozone depletion can then take place in the lowest few km of the stratosphere [Solomon *et al.*, 1998].
- UARS satellite data were used to infer the heat budget of the stratosphere, determine radiative relaxation time scales, and obtain estimates of the mean meridional circulation via a diabatic circulation calculation. The results are compared with those obtained over a decade ago from NIMBUS-7/LIMS observations. A climatology derived from the calculations has been made available on the World Wide Web [Mertens *et al.*, 1999; Mlynczak *et al.*, 1999].

Publications

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The Use of a Two-Dimensional Model for Understanding Past Ozone Downward Trends and Future Ozone Recovery

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Research Objectives

The objective of this research is to use a fixed transport two-dimensional (altitude and latitude) model of the atmosphere to investigate natural and mankind caused variations in atmospheric constituents with special focus on stratospheric ozone. Constituent variations caused by ultraviolet flux, volcanic eruptions, relativistic electron precipitation events, solar proton events, transport variations, mankind-caused bromine and chlorine increases, future supersonic civilian transport planes, and Space Shuttle and rocket launches were all studied.

Summary of Progress and Results

Substantial improvements have been made to our two-dimensional (2-D) model in the 1997-1999 time period, especially in the model's representation of atmospheric transport. The chemical reaction rates were also updated to be consistent with JPL-97 (DeMore *et al.*, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Jet Propulsion Laboratory Publication 97-4, January 15, 1997).

We quantified the natural ozone variations caused by solar cycle changes and sulfate aerosol density variations along with the humankind-caused decreases over the 1979-1992 time period and compared them with satellite measurements. We then evaluated uncertainties in our predictions of the total ozone changes over this period using a Monte Carlo technique to propagate input reaction rate uncertainties in our 2-D model. Most of the features of the globally and annually averaged observed total ozone change between 1979 and 1992 are well within the computed uncertainties of the modeled changes. However, the seasonal variations in the Northern Hemisphere middle and high latitude observed ozone trend are not well simulated within the model predicted uncertainties. This disagreement indicates a problem in our model formulation, which requires further investigation.

We investigated the seasonal and long-term changes in mesospheric water vapor and found fairly good agreement between the observations and our 2-D model simulations. Solar cycle variations in Lyman alpha (121.6 nanometer wavelength), responsible for photodissociating water vapor, cause long-term (several year) changes in water vapor of 30-40% at 80 km. These solar cycle induced variations make it fairly difficult to detect an anthropogenically-caused change in mesospheric water vapor.

We studied the impact on the stratosphere of the historical launch rate of the Space Shuttle, Titan III, and Titan IV rockets. We included emitted chlorine compounds and aluminum oxide (alumina) particles in these computations. The largest predicted decrease of 0.025% in annually averaged global total ozone was in year 1997 with about two-thirds of this predicted change resulting from the emitted chlorine compounds and about one-third resulting from the emitted alumina.

We did a thorough evaluation of our new model transport formulation, and found mostly good agreement with a wide range of long-lived tracer observations. We found that the new transport methodology provided a substantial improvement in tracer simulations compared to previous versions of the model transport.

We used our 2-D model in support of international and national assessments of ozone depletion caused by mankind-produced halogens and a possible future high-flying supersonic civil transport fleet of aircraft. We participated in an intense model and measurement intercomparison, which tested the ability of models to predict a wide range of atmospheric tracers and ozone related constituents. We obtained reasonably good agreement in a variety of model-measurement comparisons of tracers and chemically active constituents.

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3-D Models of Tropospheric Chemistry

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Research Objectives

The general goal of this project is to improve knowledge of the chemistry of the troposphere through the development and application of global 3-D models. Our present emphasis is on understanding human impacts on tropospheric ozone. Tropospheric ozone is of considerable environmental importance as the primary precursor of OH (the main atmospheric oxidant), as a greenhouse gas, and as a toxic air pollutant. Ozone is produced in the troposphere by photochemical oxidation of CO and hydrocarbons in the presence of nitrogen oxides (NO_x). Our ongoing research focuses on (1) the factors controlling ozone in the tropical troposphere, (2) the effect of increasing Asian emissions, and (3) the causes of the long-term trends in ozone and CO observed over the past decades. We use a new global 3-D model of tropospheric ozone- NO_x -hydrocarbon chemistry driven by assimilated meteorological observations from the NASA Goddard Earth Observing System (GEOS). The model is being applied to the analysis of a large ensemble of in situ and space-based data sets. Over the next few years we will take advantage of a number of new space-based data sets for atmospheric CO, lightning, and biomass burning.

Summary of Progress and Results

Over the past three years we have used our mature global 3-D model of tropospheric chemistry driven by meteorological fields from the Goddard Institute of Space Studies (GISS) general circulation model to address a number of issues related to tropospheric ozone. In parallel we have developed an improved, higher-resolution model driven by GEOS meteorological observations. We have submitted results from both models to the IPCC 2001 model intercomparison.

We applied the Harvard-GISS model to investigate the factors controlling the global-scale distribution of tropospheric ozone. We found that the ozone budget is dominated globally by chemical production and loss within the troposphere, and that these two terms are in close balance at all latitudes except polar winter. The contribution of transport from the stratosphere to tropospheric ozone is about 20% at mid-latitudes and 5% in the tropics. The observed ozone

spring maximum in the remote Northern Hemisphere is well reproduced by the model, where it is caused in part by transport from the stratosphere and in part by long-range transport of ozone pollution.

We used the model to examine the export of ozone and NO_x from the United States to the global atmosphere and to track the global influence of fossil fuel combustion on NO_x. We found that 20% of fossil fuel NO_x in the United States is exported from the boundary layer as NO_x or peroxyacylnitrates (PANs), primarily to the North Atlantic. The United States contribute half of fossil fuel NO_x over the North Atlantic while China contributes half of fossil fuel NO_x over the North Pacific. We also used the model to examine the effect of rapid industrialization in eastern Asia on surface ozone in the United States. We found that rising Asian emissions from 1985 to 2010 should increase ozone concentrations by 2-6 ppbv in the western United States in spring-summer, more than offsetting the benefits of 25% domestic emission controls.

In another application, we investigated the changes in tropospheric ozone and OH since 1850 due to anthropogenic emissions. Our results indicate a 60% global increase in tropospheric ozone and a 9% decrease in global mean OH. We also examined trends in tropospheric ozone at northern midlatitudes for 1970-1996 by analysis of ozonesonde data. We found decreasing or zero trends over North America, and increases over Europe and eastern Asia; we are now using the Harvard-GISS model to examine the causes of these trends.

In parallel to the above applications, we are developing the Harvard-GEOS model as a flexible tool for tropospheric chemistry simulations. Initial development and evaluation of the ozone-NO_x-hydrocarbon model is now complete. We are applying this model to simulation of the PEM-West B aircraft mission (February-March 1994), using meteorological data for that period. Our goals are to quantify the export of ozone and its precursors from the Asian continent, and to understand the subsequent chemical aging over the ocean. We find that the model can reproduce the principal features of the Asian outflow observed in PEM-West B.

We are also applying the Harvard-GEOS model to analyze interannual variability and trends of CO over the past decade. Our first step has been to develop an improved polynomial parameterization for rapid computation of OH in the model. This parameterization is now being tested with single-year simulations.

Other ongoing projects with the Harvard-GEOS model include:

- Simulation of ozone pollution over the United States to determine the influence of exogenous sources;
- Simulation of ²¹⁰Pb/⁷Be to design and test a wet scavenging algorithm for soluble tracers;
- Development of methyl iodide as a tracer of marine convection in global 3-D models; and
- Simulation of HCN as a potential biomass burning tracer detectable from space.

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Use of SAGE-II Observations in Two-Dimensional Chemistry-Transport Models

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Research Objectives

Our participation in the SAGE-II Science Team during the April 1996 to March 1999 period had the following goals: (1) to compare model results to SAGE II data, in order to assess gaps in our understanding of stratospheric processes (chemical, dynamical, and microphysical) affecting aerosol growth and ozone chemistry; (2) to compare our model results with data products by other science team members; (3) to utilize SAGE-II data, in conjunction with data from UARS and/or relevant aircraft data, to test current mechanisms for ozone chemistry, heterogeneous chemistry, aerosol growth, and transport utilized in current 2-D assessment models; (4) to study stratospheric transport between the tropics and midlatitudes using SAGE II ozone data as well as N₂O and CH₄ from ATMOS and other sources; and (5) to participate in the theory portion of the POLARIS (Photochemistry of Ozone Loss in the Arctic Region in Summer) ER-2 campaign in 1997.

Summary of Progress and Results

The AER 2-D Sulfate Model: Heterogeneous reactions occurring on the surfaces of sulfate aerosols play a crucial role in determining the ozone behavior in the lower stratosphere. Therefore a key component of this work was to use the SAGE data to refine and validate the AER 2-D sulfate aerosol model. The AER sulfate aerosol model, which was developed in collaboration with Dr. Glenn Yue at NASA Langley, employs the framework of the AER 2-D chemical transport model, along with the chemistry of sulfur compounds and the microphysics of sulfate aerosols, to predict aerosol concentrations in 40 size bins ranging from 0.39 nm to 3.2 μm [see Weisenstein *et al.*, 1997]. An important model enhancement under this contract was the implementation of a temperature probability approach to account for the effects of longitudinal and temporal variations in temperature on homogeneous nucleation rates and temperature-dependent reaction rates. A comparison of model-calculated aerosol parameters with SAGE and SAGE II observations for background periods is given in Weisenstein *et al.* [1997]. Those results indicate that transport of SO₂ from the tropical upper troposphere into the stratosphere plays a significant role in the sulfur budget of the lower stratosphere and adds significantly to the formation of new particles in the cold tropical tropopause region. Though stratospheric aerosol mass and surface area calculated by the model agree well with SAGE data, the aerosol extinction

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at 1.0 μm was found to be a factor of two lower than SAGE observations for nonvolcanic periods. A simulation of the effects of the Mt. Pinatubo eruption was performed with a one-time injection of 20 megatons of SO_2 on June 15, 1991. The calculated aerosol mass in the stratosphere peaked at 32.7 megatons four months after the eruption, in reasonable agreement with observations from SAGE II, AVHRR, and ISAMS. The calculated e-folding time for aerosol decay in the whole stratosphere was 8.4 months in the model, as compared with 11.4 months from the SAGE II data for the December 1992 to June 1993 period [Weisenstein *et al.*, 1997]. Another application of the AER sulfate aerosol model was for assessment of the effects of aircraft sulfur emissions [Weisenstein *et al.*, 1998]. It is found that sulfur converted to small particles in the plume has a much greater global impact than sulfur which remains as SO_2 until plume dilution. The calculated aerosol surface area perturbation for several supersonic aircraft scenarios was calculated by the AER model and used in the IPCC and NASA assessment reports on aircraft impacts.

Study of NO_y Partitioning: A study was conducted by Danilin *et al.* [1999] using a diurnal steady state photochemical box model constrained with UARS data and aerosol surface area data derived from the SAGE II instrument to analyze nitrogen species partitioning in the post-Pinatubo period (January 1992 to September 1994). The model was found to capture the general features of the nitrogen species partitioning in the post-Pinatubo years, such as recovery of NO_x following the eruption, but to underestimate the NO_2 content. Though HNO_3 column content generated by the model agreed with UARS observations at 45°S, NO_2 column was low at the same place, suggesting some problems with the model's nitrogen species partitioning.

Participation in the POLARIS Campaign: AER participated in the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) ER-2 campaign. Malcolm Ko was in Fairbanks, Alaska for the deployment of the POLARIS Campaign in May and July of 1997. Jose Rodriguez joined the September 1997 deployment. One focus of the data analysis was the NO_x/NO_y ratio, which was found to be larger than that calculated using a constrained photochemical model at high northern latitudes in summer. Recent measurements of rate constants for the reactions $\text{OH}+\text{NO}_2+\text{M}$ and $\text{OH}+\text{HNO}_3$ are found to reduce the model/measurement disagreement and alter the relative importance of the ozone catalytic loss cycles [Gao *et al.*, 1999].

Use of ATMOS and Other Data to Characterize Transport in the Stratosphere: The work of Hope Michelsen has shown that transport between subtropical and mid-latitude regions is limited, except in isolated locations. This analysis was based on geographic distributions of long-lived tracers, e.g., CH_4 and N_2O , and their relative abundances with respect to one another [Herman *et al.*, 1998; Michelsen *et al.*, 1998a]. An extension of these studies used measurements of the relative distributions of O_3 and N_2O to determine the contributions of photochemistry and dynamics to tropical O_3 laminae and their lifetimes [Jost *et al.*, 1998]. Comparisons of SAGE II ozone measurements with those of ATMOS, MLS, HALOE, and POAM were performed. SAGE II maps of ozone display similar features to those of the other instruments, and comparison of coincident occultations selected in time and space show excellent agreement. It is also shown that SAGE II aerosol parameters can be used as a tracer in the lower stratosphere to distinguish between air from inside and outside the polar vortex [Michelsen *et al.*, 1999a]. Studies of heterogeneous chemistry in the lower stratosphere have shown that aerosol-mediated reactions are likely to influence the partitioning of inorganic

chlorine (Cl_y) and reactive nitrogen (NO_y) species at temperatures between 200 and 210 K, even under low to moderate aerosol loading ($<10 \mu\text{m}^2/\text{cm}^3$) [Webster *et al.*, 1998; Michelsen *et al.*, 1999b].

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Partitioning of NO_y

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Coupling Processes Between Atmospheric Chemistry and Climate

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Research Objectives

The overall objective of this project is to improve the understanding of coupling processes among atmospheric chemistry, aerosol and climate, all important for quantitative assessments of global change. Among our priority are changes in ozone and stratospheric sulfate aerosol, with emphasis on how ozone in the lower stratosphere would respond to natural or anthropogenic changes.

The work emphasizes two important aspects:

- AER's continued participation in preparation of, and providing scientific input for, various scientific reports connected with assessment of stratospheric ozone and climate. These include participation in various model intercomparison exercises as well as preparation of national and international reports.
- Continued development of the AER three-wave interactive model to address how the transport circulation will change as ozone and the thermal properties of the atmosphere change, and assess how these new findings will affect our confidence in the ozone assessment results.

Summary of Progress and Results

Refinements Made to the AER 2-D Chemistry Transport Model and Sulfate Model

- Uses zonal temperature distribution to compute effective zonal-mean PSC surface area and heterogeneous reaction rate constants.
- Increased vertical resolution to 1.2 km and horizontal resolution to 5 degree latitude.
- Combine the sulfur model and chemistry model so that we can study the effect of sulfur species on other trace gases (e.g. volcanic SO₂ on OH).
- Updated rate constants according to JPL-97.

Transport Rates in the Atmosphere

- Performed a study that establishes a relation between values of K_{yy} used in a 2-D model and mixing rates across the subtropical barrier.
- Used different transport circulations in the AER 2-D model to study the sensitivity of ozone response. Circulations used include stream function from the GSFC 2-D model, the LLNL 2-D model, diabatic circulations using heating rate from NCEP and heating rates calculated using UARS data.
- Compared mean age of air calculated from the 2-D model with values derived from SF₆ observations.

Chlorine and Bromide Loading in the Atmosphere

- Participated in a study that used aircraft measured concentration of halocarbons to derive bromine loading in the lower stratosphere.
- Performed a model study that shows that bromine/chlorine radicals produced by short-lived source gases in the troposphere can be transported to the stratosphere in sufficient amount to affect the ozone depletion potential of those source gases. This cautions that ozone depletion potential calculated by 2-D models for short lived source gases may have underestimated this effect.

Chemistry Partitioning in the Atmosphere

- Participated in a study that shows that updated rate data is needed to correctly compute the NO_x/NO_y ratio in the lower stratosphere.
- Performed study to compare model calculated partitioning of the nitrogen species with the UARS data.

Work Related to Ozone Assessment

- Performed a study to update the ozone depletion potential of CH₃Br based on its atmospheric lifetime and new rate constants for bromine reactions in JPL-97.
- Participated in a study with the National Research Council Committee on Halon replacement chemicals used in fire fighting equipment in Naval applications.
- Provided model results to the modeling chapter of the 1998 WMO Ozone Assessment Report and participated in preparation of Chapter 1 and Chapter 2 of the report.
- Participated in the preparation of the IPCC Assessment on Effect of Aviation.
- Participated in an EPA workshop on ozone depletion potential of short-lived source gases, March 1999.

Model and Measurement Workshop

- Provided model results and participated in the Workshop.
- Helped edit the final draft of the full report.

Ozone Climate Coupling

- Performed a study to illustrate that ozone recovery may not keep pace with decrease in chlorine loading if the stratosphere cools due to increases in greenhouse gases.
- Performed studies to quantify the contribution of ozone depletion in the past decade to changes in radiative forcing.
- Used the AER 3-wave interactive 2-D model to study climate-chemistry coupling.

Modeling Studies Using Three-Dimension Tracer Model: Through our collaboration with Professor Michael Prather, we were given access to the $8^\circ \times 10^\circ$ versions of the GISS 3-D CTM for the troposphere and the stratosphere. We used the models to perform the following studies:

- Used the tropospheric version of the model to predict the accumulation of trifluoroacetic acid from degradation of HFC-134a in the atmosphere.
- Used the tropospheric model to study the mercury budget, giving deposition rates from current emissions.
- Used the stratospheric version of the model to study the distribution of aluminum oxide particles from solid rocket exhaust associated with the Space Shuttle launches.

Publications

Transport in the Stratosphere

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Ozone/Climate Coupling

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Tropospheric Trace Gas Interactions with Aerosols

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Research Objectives

Tropospheric aerosols are of considerable environmental importance. They modify the radiative budget of Earth by scattering and absorbing radiation, and by providing nuclei for cloud formation. Additionally, they provide surfaces for heterogeneous and multiphase reactions that affect tropospheric chemistry. For example, Dentener and Crutzen [1993] showed that reactions of N_2O_5 and NO_3 with sulfate aerosols may significantly alter the tropospheric concentrations of NO_x , O_3 , and OH by converting NO_x to HNO_3 which is rapidly removed by precipitation. Zhang *et al.* [1994] assumed these same reactions would occur on dust aerosols and showed that dust outbreaks may reduce NO_x levels by up to 50%. Dentener *et al.* [1996] studied the possible effect of reactions on dust on sulfate, nitrate, and O_3 concentration. Heterogeneous and multiphase reactions on aerosols may also perturb the sulfur cycle the chlorine cycle and the bromine cycle. Because these reactions can release free chlorine and free bromine they might lead to the destruction of ozone in the marine boundary layer that may be important to include in models of tropospheric chemistry. The goal of our proposed work is to couple our global aerosol and ozone models in order to examine the role of heterogeneous and multiphase reactions in the tropospheric cycles of ozone and NO_x . Coupling our prognostic aerosol model with our ozone model will also allow us to examine how homogeneous chemistry can affect aerosol composition.

Summary of Progress and Results

We have initially examined the coupling between HNO_3 , NH_3 , and sulfate aerosol using a box-model simulation. We used the multi-component, size-resolved aerosol chemistry box model described by Jacobson [1996] and updated in Jacobson [1999]. This model simulates inorganic chemistry in a system consisting of sulfate, nitrate, ammonium, chloride, sodium, organic carbon, elemental carbon, dust, and water. We applied the model under the assumption that sulfate, nitrate and ammonium are internally mixed. The major assumption in this application is that the aerosol is at thermodynamic equilibrium with the gas phase. We first specified the size distribution of aerosol sulfate into 10 size bins. Then the aerosol chemistry model was used to calculate the gas/aerosol partitioning for nitrate and ammonium, so that chemical equilibrium was maintained in each size section. The take-up of water by each size section as a function of relative humidity was also modeled.

We examined the uptake of gas phase HNO_3 and NH_3 by sulfur aerosols for different molar ratios of NH_3 to H_2SO_4 and for different molar ratios of HNO_3 to H_2SO_4 . Because the model-predicted molar ratios of both total ammonia to sulfate and total nitrate to sulfate can exceed four to one during winter, substantial amounts of NH_3 and HNO_3 , partition into the aerosol phase. In summer, molar ratios for both components tend to be less than 2. Under these conditions, in winter, more than 50% of the total nitrate (and up to 85%) is partitioned to the aerosol phase. In summer, if molar ratios are near 2 to 1 then 30% of the total nitrate can be in the aerosol phase.

To examine the effect of different conditions more fully, we initialized a global scale version of the aerosol chemistry model using the three-dimensional monthly average distributions of aerosol sulfate [Chuang *et al.*, 1997; Penner *et al.*, 1994] and the predicted HNO_3 [Penner *et al.*, 1994] from previous simulations of the GRANTOUR model [Walton *et al.*, 1988; Penner *et al.*, 1991]. We also obtained monthly average concentrations of NH_4^+ plus NH_3 from the model of Dentener and Crutzen [1993]. We are now preparing a manuscript discussing these results.

These results point to the importance of coupling tropospheric chemistry models with aerosol models. Nitrate partitioned to the aerosol phase will undergo different scavenging and deposition processes than nitrate partitioned only in the gas phase. Thus, it is important to continue to develop the capability to treat the coupling between aerosol and gas phase chemistry.

Publications

Includes publications from our previous NASA-ACMAP sponsored research: Global Studies of the Sulfur Cycle Including the Influence of DMS and Fossil Fuel Sulfur on Climate and Climate Change which was funded during 1997.

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Coupling Atmospheric Circulation and Chemistry: Developing Chemistry-Transport Models for Climate Simulations

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Research Objectives

A 3-year program of research—a continuing collaboration between Goddard Institute for Space Studies (GISS), Harvard, and University of California, Irvine (UCI)—has developed more accurate, versatile, and user-friendly global chemistry-transport models (CTMs). A key to this project was working with the atmospheric dynamics models to diagnose and couple the meteorological fields with the processes represented in CTMs. Chemical trace species are transported and transformed in the atmosphere by a variety of events diagnosed in the met-fields such as winds, convection, clouds, precipitation, sunlight, and turbulence. The primary connection here is with the new GISS II-prime model, and the secondary, with the EC model through the University of Oslo. A single CTM that uses archived met-fields from both climate models (GISS) and assimilated / forecast observations (EC forecasts) was developed and is currently running both tropospheric and stratospheric simulations. In addition, UCI continues to develop simplified but efficient chemical modules that can be used in long-term climate simulations. In particular, we have developed simple photochemical models based on a linearization about the current atmosphere and shall use this with the new CTM to study chemical coupling and modes through numerical experiments. This simplified chemical model will also be used within the GISS stratosphere-troposphere model to follow the evolution of the 21st century climate and the possible changes in ozone and greenhouse gas lifetimes based on a changing circulation.

Summary of Progress and Results

This period saw the completion of the theoretical/analytical basis for the definition of natural modes (eigenvectors) in CTMs. The trilogy of short papers finished (*Science*, 1998) with the demonstration of how the transport, local chemistry, and UV-radiation feedbacks created a long-lived coupled pattern in stratospheric N₂O, NO_y, and O₃. This 100-year global pattern could even be excited by a solar proton event. The idea that perturbations to short-lived gases such as ozone or NO_x could manifest themselves as long-lived, climatically important perturbations is a relatively new concept that began with this set of papers on natural modes and times scales in atmospheric chemistry. Currently, research supported under this project has demonstrated the existence and defined the pattern of the long-lived tropospheric chemical mode that we would associate with CH₄ - although the mode includes changes in O₃, CO, NO_x and all chemical

species. The mode has derived from the new UCI CTM with full tropospheric chemistry, and its excitation has been demonstrated (and quantified) with perturbations ranging from added CH₄ to aviation NO_x ('Excitation of the primary tropospheric chemical mode in a global CTM', Wild and Prather, in draft form for *JGR*).

Significant effort at UCI has gone into developing two unique general modules for CTMs. First is Fast-J, a general photolysis code for accurate calculation of photolysis rates (J's) in tropospheric CTMs including clouds and aerosols. This optimized Mie scattering code predicts the radiation field both in-cloud and below-cloud, and allows for a realistic mix of scattering and absorbing aerosols and clouds, including high-altitude ice clouds. It is general in that new cross-sections can be added, and it is efficient in only adding about 10% to the computational time ('Fast-J: Accurate simulation of in- and below-cloud photolysis in global chemical models' Wild, Zhu, and Prather, submitted to *JAC*). Second is a linearized stratospheric chemistry describing ozone. This module has finally been debugged and tested with the paper in preparation ('Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux', McLinden *et al.*, in prep for *JGR*). The recent updates to stratospheric chemistry have greatly improved the simulations of ozone with this simplified chemistry. This documented and tested module is important for the GISS climate simulations in that it allows for an interactive response of stratospheric ozone in climate runs and for CTMs that need a 'reasonable' upper boundary for their tropospheric ozone modeling.

The application of linearized chemistry of the stratospheric source gases in the UCI stratospheric CTM [Avallone and Prather, 1997] has demonstrated the relationship between trace-gas correlations and lifetime for the first time in a self-consistent 3-D model. The CTM was also used to show the impossibility of large sources of extra-terrestrial water from comets [Hannegan *et al.*, 1998].

This program has supported participation in international assessments, both ozone and climate evaluations. The recent climate assessments spawned a pair of multi-authored papers from the model intercomparisons [Jacob *et al.*, 1997; Olson *et al.*, 1997]. Substantial effort also went into the recent aviation assessment that presented the first comprehensive evaluation of the climate impacts of the global aircraft fleet [Prather *et al.*, 1999]. Three doctoral students have been supported over this period, with one completed thesis [Hannegan, 1999].

Publications

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Interpretation of Trace Gas Data Using Inverse Methods and Global Chemical Transport Models

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Research Objectives

This grant supports a global 2-D/3-D atmospheric chemistry/transport modeling and data-analysis project devoted to inverse methods for determining regional and global transient source and sink strengths for trace gases important in ozone depletion and the greenhouse effect.

Summary of Progress and Results

Most of the work has been published in fourteen peer-reviewed papers. The research accomplishments are divided conveniently into five categories:

- *Three-Dimensional Modeling:* we have, in collaboration with NCAR scientists, successfully developed and tested a global three-dimensional Model for Atmospheric Transport and Chemistry (MATCH) [Mahowald *et al.*, 1997a, b; Rasch *et al.*, 1997]. We also examined the impact of the vertical profile of the horizontal wind in the troposphere and lower stratosphere on the vertical convective transport of chemical species [Wang and Prinn, 1998].
- *Time-Variable Regional Source-Sink Determinations Using Inverse Methods in 3-D Models.* In addition to the work on CCl₃F by Mahowald *et al.* cited above, a new method for estimating time varying fluxes of atmospheric trace gases using observations and 3-D transport models has been investigated [Mulquinen and Norton, 1998; Mulquinen *et al.*, 1998].
- *Lifetimes and Emissions of Present and Alternative Halocarbons:* analysis of the extensive ALE/GAGE/AGAGE observations (1978-present) of trace gases using our inverse methods with a 2-D model was supported in part by this grant as well as by the separate grant to MIT. We have measured the atmospheric trend and deduced the lifetime of CHF₂Cl (HCFC-22) and thus obtained an independent estimate of OH concentrations in statistical agreement with that derived from CH₃CCl₃ [Miller *et al.*, 1998]. We have also measured the trends and deduced the emissions of CF₃CHF₂ (HFC-134a), CCl₂FCH₃ (HCFC-141b) and CCIF₂CH₃ (HCFC-142b) [Simmonds *et al.*, 1998]. We continued work on optimal estimates of lifetimes and/or emissions for CFCl₃ (CFC-11), CF₂Cl₂ (CFC-12), and CCl₄ [Cunnold *et al.*, 1997; Simmonds *et al.*, 1998b].

- *Parametric Uncertainty Analysis:* with support from this grant, we have developed at MIT a new powerful method for deducing the probability distribution functions (PDFs) of model outputs given the PDFs of uncertain inputs/parameters [Tatang *et al.*, 1997]. This method has been applied to uncertainty analysis of the direct and indirect radiative forcing by anthropogenic sulfate aerosols [Pan *et al.*, 1997, 1998].
- *Inverse Methods in Global Biogeochemical Cycles:* the growing realization of the power of inverse methods in studies of chemical fluxes led to the 1998 “Workshop on Inverse Methods in Global Biogeochemical Cycles.” The PI gave the opening lecture entitled “The measurement equation for trace chemicals in fluids and solution of its inverse using optimal linear filtering.” The peer-reviewed lectures (including the PIs) from this Workshop are now in press in *Geophysical Monographs* [Prinn, 1999].

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Systematic Assessment and Analysis of Two-Dimensional Stratospheric Ozone Models**Principal Investigator:** Herschel Rabitz**Organization:** Department of Chemistry
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The objective in this program was to explore the relationship between stratospheric ozone profiles and the various underlying chemical and physical processes. The research addressed this issue by development and exploitation of advanced model analysis techniques. The research started with linear sensitivity analysis tools combined with Monte Carlo sampling and proceeded to the development of a new non-linear high dimensional model representation (HDMR) procedure. The procedure was successfully tested for the treatment of chemical kinetics and radiative transport. This latter research forms the groundwork for the continued development of HDMR as a set of highly efficient tools to accelerate atmospheric modeling.

Summary of Progress and Results

- *An Efficient Chemical Kinetics Solver Using High Dimensional Model Representation:* A high dimensional model representation (HDMR) technique was introduced to capture the input-output behavior of chemical kinetic models. The HDMR expressed the output chemical species concentrations as a rapidly convergent hierarchical correlated function expansion in the input variables. In this research, the input variables were taken as the species concentrations at time t_i and the output was the concentrations at time $t_i + \delta$, where δ can be much larger than conventional integration time steps. A specially designed set of model runs was performed to determine the correlated functions making up the HDMR. The resultant HDMR can be used to (1) identify the key input variables acting independently or cooperatively on the output, and (2) create a high speed fully equivalent operational model (FEOM) serving to replace the original kinetic model and its differential equation solver. A demonstration of the HDMR technique was done for stratospheric chemical kinetics. The FEOM proved to give accurate and stable chemical concentrations out to long times of many years. In addition, the FEOM was found to be orders of magnitude faster than a conventional stiff equation solver. This computational acceleration should have significance in many chemical kinetic applications.

- *Radiation Transport Simulation by Means of a Fully Equivalent Operational Model:* The radiation transport component of atmospheric modeling codes is typically a major contributor to the overall execution time. This research introduced a fully equivalent operational model (FEOM) as a high-speed replacement for traditional transport modules. The input information to the FEOM was the atmospheric trace gases and temperature profiles as a function of altitude, as well as the surface temperature and albedo. The FEOM operated by identifying how these latter variables impacted the heating rate as a function of altitude. This relationship was compactly represented by the FEOM in terms of a hierarchy of cooperativity relations amongst the input variables, thereby producing an accurate equivalent module. In the present test of the concept, water vapor and temperature were treated as altitude dependent inputs, and the FEOM was shown to be better than 97% accurate over a broad input variable range, while simultaneously being approximately 10^3 times faster than the traditional radiation transport module it replaced.
- *Efficient Input-Output Model Representations:* In this research, a family of multivariate representations was presented to capture the input-output relationships of physical systems with many input variables. The high dimensional model representations (HDMR) were based on the ansatz that for most physical systems, only relatively low order correlations of the input variables will have an impact on the output. Application of the HDMR tools can dramatically reduce the computational effort in representing the input-output relationships of a physical system. Two types of HDMRs were presented in this research: ANOVA-HDMR is the same as the analysis of variance (ANOVA) decomposition used in statistics. Another cut-HDMR was shown to be computationally more efficient than the ANOVA decomposition. Three test examples were done to illustrate the high computational efficiency of cut-HDMR.
- *Chemical Reaction Rate Sensitivity and Uncertainty in a Two-Dimensional Middle Atmospheric Ozone Model:* The NASA Goddard Space Flight Center two-dimensional (2-D) model was used to study the sensitivity of model ozone concentrations to input chemical reaction rates, and the uncertainty of the model-calculated concentrations. Ozone sensitivity coefficients to changes in chemical reaction rates were defined as logarithmic partial derivatives of the ozone concentration with respect to the chemical reaction rates. These logarithmic derivatives were estimated using a finite difference technique. The ozone sensitivity coefficients to 96 gas phase chemical reactions in the 2-D model showed that the ozone concentration was sensitive to the rates of about 25 reactions. The magnitude of the ozone sensitivity coefficients varied from 0.05 to 0.9. The uncertainty of the model-calculated ozone was evaluated using a guided Monte Carlo (GMC) method from a probability distribution function. The GMC method judiciously combined uncertainty estimates derived from the sensitivity information with Monte Carlo runs of the model. The uncertainty of the model ozone concentration due to uncertainties in the gas phase reaction rates was calculated from published chemical rate uncertainties, and varies from 10-20% in the lower stratosphere to 30-40% in the mesosphere. The latitude-altitude distribution of the uncertainty of the model-calculated ozone was presented.

- *Risk Analysis by the Guided Monte Carlo Technique:* Risk assessment of modeling predication has become increasingly important as input to decision makers. Probabilistic risk analysis is typically expensive to perform, since it generally requires the calculation of a model output Probability Distribution Function (PDF), followed by the integration of the risk portion of the PDF. This research developed a new risk analysis Guided Monte Carlo (GMC) technique. The new technique maintained the global coverage of Monte Carlo (MC) while judiciously combining model reruns with efficient sensitivity analysis predictions, to accurately evaluate the integrated risk portion of the PDF. The GMC technique facilitated risk analysis of complex models, where the expense was previously prohibitive. The research presented two examples to illustrate the technique, its computations savings, and broad applicability. The illustrations were (1) an ordinary differential equation-based chemical kinetics model, and (2) an analytic dosimetry model. For any particular example, the degree of savings with the GMC technique depended on the relative risk being evaluated. In general, the highest fractional degree of savings with the technique occurred for estimating risk levels that were specified in the far wing of the PDF. If no savings are possible, the GMC technique defaulted to the true MC limit. In the illustrations, the GMC analysis saved approximately a factor of four in computational effort relative to that of a full MC analysis. Furthermore, the GMC technique could also be implemented with other possible sampling strategies, such as Latin Hypercube, when appropriate.

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Global Modeling of Tropospheric Trace Gases

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Research Objectives

This work has three main goals: optimizing the GISS (Goddard Institute for Space Studies) GCM (General Circulation Model) for modeling of tropospheric trace gases; providing the necessary fluxes/parameters to Harvard, UCI (University of California at Irvine) and GMI (Global Modeling Initiative) for CTM (chemical tracer model) studies; and investigating budgets of tropospheric species. The overriding aim is to improve our understanding of the interactions between climate change and chemistry. Passive tracers are being used in the course of model development to determine transport properties of concern for tropospheric chemistry, including interhemispheric transport, vertical mixing within the troposphere, and tropospheric-stratospheric exchange. Three hourly values of some 20 parameters from the model, including winds, convective fluxes, temperatures, clouds, and rainfall were saved and provided to Daniel Jacob (Harvard) and Michael Prather (UCI) for their global chemical modeling tasks. Similar parameters were saved for the GMI model (Doug Rotman). Tropospheric budgets which are being investigated include NO_y, CO₂, CH₄, CFCs and cosmogenic and radon-product isotopes for which rainout and scavenging parameterizations have been developed. Calculations of troposphere-stratosphere exchange utilize SF₆, CFC-11, bomb ¹⁴C, and mass fluxes.

Summary of Progress and Results

During the past three years we have continued to test the transport processes of the GISS GCM as each major change is implemented into the model. The rationale is to ensure that new versions of the model are suitable for tropospheric chemistry purposes and to help in model development. This has involved utilizing the on-line tracer capability, so that tracers are moved each time-step by the model dynamics, and sources/sinks incorporated each physics time step. The on-line tracers routinely used include CFC-11, ⁸⁵Kr, ²²²Rn, and ¹⁴C, SF₆, CO₂ and N₂O.

The recent focus has been on exchange between the troposphere and stratosphere, in particular the effect of altering the vertical resolution of a GCM, and processes associated with it. Four on-line tracers are employed: CFC-11 and SF₆ for mixing from the troposphere into the stratosphere, Rn²²² for vertical mixing within the troposphere, and ¹⁴C for mixing from the stratosphere into the troposphere. Four standard models are tested, with varying vertical resolution, gravity wave drag and location of the model top, and additional subsidiary models are employed to examine

specific features. The results show that proper vertical transport between the troposphere and stratosphere in the GISS models requires lifting the top of the model considerably out of the stratosphere, and including gravity wave drag in the lower stratosphere. Increased vertical resolution without these aspects does not improve troposphere-stratosphere exchange. The transport appears to be driven largely by the residual circulation within the stratosphere; associated E-P flux convergences require both realistic upward propagating energy from the troposphere, and realistic pass-through possibilities. A 23-layer version with a top at the mesopause and incorporating gravity wave drag appears to have reasonable stratospheric-tropospheric exchange, in terms of both the resulting tracer distributions and atmospheric mass fluxes. This model is now being used in the EOS/IDS CACTUS (Chemistry, Aerosols, and Climate: Tropospheric Unified Simulation) project. Results of this work are described in Rind *et al.* [1999].

Additional tests, for both exchange between the stratosphere and troposphere and stratospheric transports were made utilizing the cosmogenic radionuclides ^{10}Be ($t_{1/2} = 1.5 \times 10^6$ years) and ^7Be ($t_{1/2} = 53$ days). Both tracers are generated steadily, with maximum production occurring at midlatitudes of the stratosphere. During transport away from their source, the ratio $^{10}\text{Be}/^7\text{Be}$ increases, and thus acts as a clock for air mass age. Results of lower ratios than observed indicate an excessive leakage into the troposphere in the 9 layer model, with improvement when higher vertical resolution and gravity wave drag was included. Modeling results also indicate that observations of high ratios at high latitudes during winter imply substantial 'leakiness' of the tropical pipe in the lower stratosphere, and that additional observations of these isotopes would be quite useful [Koch and Rind, 1998].

Increased horizontal mixing within the troposphere was obtained by improving the boundary layer formulation. A paper describing this work was published by Hartke and Rind [1997].

Three hourly values of some 20 parameters, including winds, convective fluxes, temperatures, clouds, and rainfall were saved for 2 year simulated years with both the 9 and 23 layer versions of the new model. These were provided to Daniel Jacob (Harvard) and Michael Prather (UCI) for their global chemical modeling tasks, and to Doug Rotman for the GMI model.

In conjunction with the focus on interactions between climate, chemistry and aerosols, a meeting was held at GISS chaired by D. Rind bringing together researchers from these communities who are funded as a part of ACMAP (Atmospheric Chemistry Modeling and Analysis Program) and related EOS (Earth Observing System) projects. It provided a forum for the interaction between modelers and scientists providing space-based measurements. A summary of the meeting highlighting the speakers main points has been published [Kaye and Rind, 1998].

Important for both chemistry calculations and climate assessments are temperatures in the upper troposphere/lower stratosphere region. Upper tropospheric temperatures have failed to warm as expected from model simulations of greenhouse gas increases, possibly due to ozone losses in the lower stratosphere. An analysis of different observational data sets including remote sensing observations was performed by Shah and Rind [1998]. It was determined that the experimental MSU (Microwave Sounding Unit) channel 3R, of critical importance for upper troposphere temperature evaluations, is too cool by some 6°K in the tropics. Correction factors were formulated to bring its results more in line with other observational techniques.

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Stratospheric General Circulation Climate Models

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Research Objectives

This work has two main goals: to utilize the GISS Global Climate Middle Atmosphere Model (GCMAM) for studies of stratospheric climate change; and to develop the next version of the GCMAM with on-line photochemistry for coupled climate/chemistry simulations. During the past three years the GCMAM has been used for published stratospheric climate studies involving changes in stratospheric ozone, stratospheric water vapor, increased atmospheric CO₂, coupled CO₂-ozone climate change, and the effect of anthropogenic forcing on natural atmospheric variability. Additional work using the model has included effects of atmospheric contrails and aircraft radiative forcing of climate. Development has continued on the next version of the GCMAM, output of which has been used in studies involving GMI (Global Modeling Initiative)/aircraft assessments, M&M2 (Models and Measurements 2) tracer comparisons, and GRIPS (GCM-Reality Intercomparison Project for SPARC) climatological comparisons.

Summary of Progress and Results

During this time period, the GISS GCMAM has been used for a variety of stratospheric climate change studies. The effects of anthropogenic climate change on stratospheric ozone were explored in several simulations. We investigated the interplay between projected future emissions of greenhouse gases and levels of ozone-depleting halogen species. Anthropogenic effects helped produce a more stable Arctic polar vortex, with significantly colder temperatures in the lower stratosphere and concomitantly increased ozone depletion. Increased concentrations of greenhouse gases might therefore be at least partly responsible for the very large Arctic ozone losses observed in recent winters. Arctic losses reach a maximum in the decade 2010 to 2019 in our model, roughly a decade after the maximum in stratospheric chlorine abundance [Shindell *et al.*, 1998a].

In other studies, the equilibrium response of temperature and ozone to doubled atmospheric CO₂ was investigated. With increased CO₂ resulting in colder temperatures throughout the stratosphere, ozone in the upper stratosphere increased by 10-15% [Shindell *et al.*, 1998b]. The increased ozone then mitigated the stratospheric cooling by some 20%, while having little effect on surface air temperature changes [Rind *et al.*, 1998]. An important result, which influenced

polar ozone depletion, was the reduction in stratospheric warmings in the doubled CO₂ climate, caused by the reduced ability of wave 2 energy to propagate into the middle stratosphere.

Interannual variability of the Antarctic ozone hole was investigated in two modeling studies. In the first, mid-winter tropospheric wave variability was found to affect the lower stratospheric temperatures, and hence the austral spring ozone hole, with greater wave energy leading to reduced ozone losses (by about 20%) [Shindell *et al.*, 1997]. In the second, the QBO (quasi-biennial oscillation) changed the refractive path of planetary waves, again altering lower stratospheric temperatures and Antarctic ozone hole magnitudes, by some 40% between QBO extremes [Shindell *et al.*, 1999a]. Circulation changes were also found to be responsible for seasonal and interannual variability of N₂O and CFC budgets [Wong *et al.*, 1999].

The effect of solar forcing on the troposphere/stratosphere system was investigated in two modeling studies. Five percent variations in solar ultraviolet (UV) radiation were able to reproduce the observed enhanced subtropical ridge in the upper troposphere and lower stratosphere in one such study [Balachandran *et al.*, 1999]. Similarly, realistic UV variations, when combined with calculated ozone changes, were also able to simulate aspects of these observations [Shindell *et al.*, 1999b]. Both studies therefore support the reality of observed solar cycle effects on the atmosphere.

Anthropogenic effects may also be altering the natural variability patterns in the atmosphere, through their influence on the stratospheric circulation. Modeling studies showed that only by inclusion of a full stratosphere was it possible to reproduce the observed change in the phase of the Arctic oscillation, which is associated with the pattern of temperature changes observed during the last several decades. Anthropogenic effects help alter the zonal wind patterns in the stratosphere, which then affect planetary wave propagation and tropospheric circulations [Shindell *et al.*, 1999c]. The influence of the Antarctic ozone hole on stratospheric dynamics was explored by Wong [1998], who showed that the lower stratospheric radiative temperature cooling from the ozone loss was partly counteracted by dynamical warming due to planetary wave and residual circulation changes.

The middle atmosphere model has recently been used to investigate the effect of aircraft contrails on climate (in work partly supported by the Subsonic Assessment of the Atmospheric Effects of Aviation Program). Results show that altering high level cloud cover along aircraft flight paths by 1% changes the global mean surface air temperature by about 0.4°C in the model. Estimated current changes of 0.1% would not be observable in the temperature record, but if projections for the next 50 years are accurate, the contrail effect should become observable relative to the noise in MSU temperature observations [Rind *et al.*, 1999]. The PI was also a lead author for the chapter on the potential climate change from aviation in Aviation and the Global Atmosphere (IPCC, 1999), which involved numerous calculations of the radiative effects of aircraft perturbations, utilizing the GCMAM.

The new version of the GCMAM was used to assess how much water would likely be added by cometary influxes [Hannegan *et al.*, 1998]. Output from this model has now been provided to various assessment programs, including M&M2, in which it was shown that it provides the most realistic age of air (in the UCI model; Hall *et al.*, *JGR*, 104, 1999, p. 18822), the GRIPS comparison, which showed that it produced quite realistic wind and temperature climatologies,

but with too low interannual variability (Pawson *et al.*, submitted to *Bull. Amer. Meteor. Soc.*) and the GMI model for aircraft impact assessment.

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Assimilation of Ozone Data for Global Change Studies

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Research Objectives

The objectives of this research is to investigate whether ozone observations from different instruments can be assimilated in a predictive ozone model to generate a three-dimensional ozone climatology suitable for interannual and process studies.

Summary of Progress and Results

A near real-time ozone data assimilation system has been developed and will be used to support the science goals of the Earth Observing System (EOS) Terra mission. This will be the first routinely produced assimilated ozone product released for general scientific use. The ozone assimilation system utilizes ozone observations from both the Total Ozone Mapping Spectrophotometer (TOMS) and the Solar Backscattered Ultraviolet (SBUV) instrument to generate global synoptic maps of ozone that are archived at six-hour intervals. These instruments were chosen because they are available in near-real time and form the backbone of the long-term data record. The validation of the ozone assimilation system shows that the assimilated product agrees well with independent Halogen Occultation Experiment (HALOE) and ozonesonde observations. The initial application of this product is to provide ozone fields to assist in the ‘atmospheric corrections’ that are necessary for the retrieval of information from other NASA instruments, however, the quality of validation experiments suggest that the product is of sufficient quality to be extended to other applications.

The applications being considered include estimates of tropospheric ozone, provision of ozone fields for interactive retrievals, use of analysis increments from the assimilation to evaluate model performance, and development of long-term consistent three-dimensional global ozone fields. The results from exploratory studies are promising. For instance, in the troposphere the root mean square difference between the assimilation analysis and concurrent ozonesondes is approximately 50%. This suggests that the assimilation provides a viable and competitive method to produce estimates of tropospheric ozone. Also, we are currently introducing the analyzed ozone fields into the meteorological assimilation to assure greater consistency with the temperature and wind observations.

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Chemistry-Climate Coupling in a GCM with Simplified Tropospheric Chemistry**Principle Investigator:** Drew Shindell**Organization:**
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The main goal of this work is to further develop and use a fast tropospheric chemistry model for online use in the GISS general circulation model (GCM) to study climate-chemistry interactions. Our model includes detailed emissions of source gases (NO_x , CH_4 , and CO), the complete dynamics and cloud schemes present in the GCM, and a simple chemistry model based on the chemical family technique using only a small subset of tropospheric species. We have found that we are able to reasonably simulate the behavior of tropospheric ozone using only $\text{HO}_x\text{-NO}_x\text{-CH}_4\text{-CO}$ chemistry. This reduced chemistry only adds ~30% to the running time of the GCM, in contrast to more sophisticated chemistry packages which take much longer than the GCM itself.

This work has been closely coordinated with the in progress Earth Observing System Interdisciplinary Science (EOS/IDS) Chemistry-Aerosol-Climate in a Tropospheric Unified System (CACTUS) project of Harvard, GISS, GSFC, Irvine, and CalTech, to develop a more complete chemistry package for use in the GISS GCM. To facilitate comparisons, we use the same emission sources and sinks (wet and dry deposition) as in the CACTUS model. While our model is being validated by comparison to observations, comparison with the more complete CACTUS chemistry models will allow insights into the limitations that result from the use of simplified chemistry. Though the model provides a less realistic simulation of tropospheric chemistry, its speed allows it to serve as a guide for more complete models, highlighting the most important chemistry-climate couplings, which can then be explored further with much more time consuming models. Furthermore, we have already run multiple climate simulations with our fast model, allowing us to assess sensitivity issues such as the impact of changing sea surface temperatures on atmospheric chemistry.

Summary of Progress and Results

This project has been funded for roughly 20 months thus far. During this time, we have largely completed the extensive model development phase of the work. The extremely simple model used for initial tests (from which results were presented in our original proposal) has been greatly expanded. That model included only the following molecules as transported species: O_x ($\text{O}+\text{O}^{(1)\text{D}}+\text{O}_3$), NO_x ($\text{NO} + \text{NO}_2 + \text{NO}_3$), H_2O_2 , H_2O , and CO. To these five, we have added in

the additional five species HNO_3 , N_2O_5 , HO_2NO_2 , CH_3O_2 , and HCHO as tracers. We have also completed the installation of interactive wet deposition of soluble gases, as promised in the original proposal, which is coupled to the new convection scheme in the GCM. This scheme now includes entraining and non-entraining plumes, mass fluxes proportional to convective instability, explicit downdrafts, and a cloud liquid-water scheme based on microphysical sources and sinks of cloud water which carries both water and ice. Since the wet deposition scheme is fully coupled with convection in the GCM, rainout and washout take place according to what is going on at a particular time in the GCM. Deposition of chemical species will thus respond to climate forcings when they cause changes in clouds and precipitation (previously, removal of NO_x and H_2O_2 took place based on a parameterization derived for the NASA Subsonic Aircraft Assessment intercomparison). Furthermore, we have added in the heterogeneous hydrolysis of N_2O_5 on sulfate aerosol using surface areas calculated in Dorothy Koch's sulfate model within the GISS GCM. This reaction proved critical to the model's ability to properly simulate the partitioning of nitrogen species in the dark.

We have replaced our previous photolysis code with the "FAST-J" 8-stream code of Dr. Michael Prather (University of California, Irvine), which, after testing both codes within our model, we found gave significantly better results.

For emissions, we have installed the known sources of surface CO emissions, including an isoprene source with a geographically realistic distribution. We have worked extensively on the parameterization of lightning NO_x in the GCM with Colin Price (Tel Aviv University). Since lightning is one of the major natural sources of NO_x in the troposphere, and likely the major natural source in the remote troposphere, it is important that changes in lightning activity be included in any climate change scenario or study of future tropospheric ozone. The GISS convection scheme is used to calculate both the total lightning, and the cloud-to-ground lightning frequencies interactively at each timestep of the model. Based on a comparison with the global lightning data set recently produced at NASA Marshall Space Flight Center, we have recently revised the lightning flash frequency generated by cloud overshooting events that occur during very strong convective events, primarily at Northern Hemisphere mid-latitudes (where the model's production was deficient relative to the observations). The new parameterization appears to give better results, and we have begun investigating the change in lightning frequency with increasing greenhouse gases. Preliminary results indicate a significant increase in flash frequency (up to 35% globally averaged in the Northern summer). Given the likelihood of future increases of lightning activity, it will be interesting to see the impact on ozone, and hence on the energy balance of the planet.

Chemistry is only applied in the troposphere in this model, but we include stratospheric sources for ozone and NO_x . For ozone, we keep stratospheric amounts at the observed, seasonally varying levels used in the GISS model [Hansen *et al*, 1995], and then allow the model to transport ozone into the troposphere based on the existing gradients at each time step. NO_x influx is defined as a fixed fraction of the ozone influx. We have found that a too large transport of ozone from the stratosphere to the troposphere is one of the main deficiencies in the current model. Our primary goal in future development will be to install the chemistry schemes into a model with more vertical layers and higher resolution around the tropopause, which has been shown to greatly improve stratosphere-troposphere exchange.

Validation efforts of the new model are currently under way. We are comparing model output with ozonesonde observations from 1980-1993 compiled by Dr. Jennifer Logan at Harvard University, and with the SASS data set of ozone, nitric acid, and other species compiled by Louisa Emmons at the National Center for Atmospheric Research. OH concentrations will be validated indirectly, since no global measurements are available, by calculating the lifetime of CH_3CCl_3 and comparing to observed values, as is typically done in tropospheric chemistry CTMs. Initial calculation yield a CH_3CCl_3 lifetime within the range found in other studies.

We have modeled the global distributions of ozone and other oxidizing species in the troposphere, and their chemical impacts on radiatively active gases. This provides a unique capacity to perform three-dimensional climate simulations which include the indirect effects of chemistry on greenhouse gases, while still running fairly rapidly, allowing for multiple simulations and sensitivity studies. The model has been run for pre-industrial, present day, doubled CO_2 , and IPCC projections for the year 2100. Furthermore, the model has been run for each scenario with both chemistry and climate changes alone, as well as with both, to explore each factor's influence. The model has also been run for each scenario both with and without lightning, to test its impact on the ozone distribution.

Publications

The results of the year 2100 simulations have been provided to the IPCC Third Assessment Report. Surface ozone levels over the northeastern United States have been provided to the US National Assessment, Metro-East region. Publications are currently being drafted for both of these reports, while a paper documenting the model is being prepared for submission to the *Journal of Geophysical Research*.

A Comparison of Observations and GCM Simulations of the Quasi-Decadal Oscillation

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Research Objectives

This work aims to improve the ability of general circulation models (GCMs) to simulate the response of the Earth's climate to long-term variations in solar output. Given the absence of reliable long-term measurements of solar variability, models must be validated by demonstrating their ability to accurately reproduce the well-observed short-term variability that is correlated with the Quasi-Decadal Oscillation (QDO). In addition, an accurate GCM simulation of the atmospheric response to the QDO would enable us to investigate the mechanism by which solar variability influences climate and ozone. We have therefore attempted to include the ozone chemical response to quasi-decadal solar variability along with the dynamical and radiative response of the GCM, and to compare the results with the observed changes in meteorological parameters and ozone. This work is being carried out in cooperation with Lon Hood (University of Arizona), who is providing observed ozone and temperature changes associated with the QDO as derived from satellite observations.

Summary of Progress and Results

We have performed several simulations with the Goddard Institute for Space Studies (GISS) Global Climate/Middle Atmosphere Model (GCMAM) to model the atmospheric response to the QDO. The model version used has 23 vertical layers, extending from the surface to 85 km, with 8° by 10° (lat \times long) horizontal resolution.

Several of the simulations have included a simplified calculation of stratospheric ozone variations that occur in response to solar flux variations, as well as in response to solar cycle induced temperature variations. Parameterized ozone chemical responses to variations in solar flux, temperature, and overhead ozone column were derived using an offline two-dimensional photochemical model. The two-dimensional model uses the observed flux variations as a function of wavelength from 180-500 nm, with 5 nm resolution, as provided by the Naval Research Laboratory [J. Lean, personal communication, 1997]. The same wavelength dependent solar output variation is used to force the GCM's radiative code, so that the two calculations are consistent. The chemical parameterizations are based on the assumption of photochemical equilibrium for ozone. In the upper stratosphere, where the lifetime of ozone is very short, ozone

transport is unimportant (except during the polar night), and this assumption should be valid. It will of course not be true in the lower stratosphere.

The chemical parameterizations were included online in the GCMAM, which has now been run for 20 years each at solar maximum and minimum. We found that with the inclusion of the ozone chemical response throughout the stratosphere, for the first time, a model was able to reproduce the relatively long record of geopotential height variations associated with the 11-year solar cycle; hence it implies that these oscillations are likely driven, at least in part, by solar variability [Shindell *et al.*, 1999]. Additional experiments were run without interactive ozone, but with an unrealistically large solar forcing to attempt to accommodate for this. These showed that this forcing is also able to reproduce some of the observed meteorological variability which is correlated with the solar cycle [Balachandran *et al.*, 1999]. This work also showed that the influence of the QBO on the model's response to solar forcing is also significant, and it will be included in future simulations.

Our current work is proceeding on three fronts. Firstly, we are extracting the temperature variations produced in the model when forced with realistic solar variability including the interactive ozone response. These will be compared with the temperature variations associated with solar variability derived from the Microwave Sounding Unit satellite. This will provide a further test of the current model's abilities. Secondly, we are continuing to explore possible reasons for the persistent model underestimation of ozone variability in the upper stratosphere resulting from solar cycle irradiance variations relative to that extracted from satellite observations taken by the Solar Backscatter Ultraviolet (SBUV) and Microwave Limb Sounder (MLS) instruments. A new possibility has been recently suggested, that solar cycle induced changes in circulation alter the abundance of methane in the upper stratosphere in phase with the solar cycle. This possibility is currently being investigated by simulations with our two-dimensional photochemical model. Lastly, we are beginning to install the parameterizations of ozone photochemical response to solar variability into the new version of the GISS model. This model has higher vertical and horizontal resolution, and allows the use of online tracers so that changes to ozone transport can be included interactively. This model should be ready to use by the end of 1999, though the model itself runs extremely slowly.

Publications

Balachandran, N. K., D. Rind, P. Lonergan, and D. Shindell, Effects of solar cycle variability on the lower stratosphere and the troposphere, *J. Geophys. Res.*, in press, 1999.

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Removal Process in the Boundary Layer and the Atmospheric Lifetime of Methyl Bromide

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Research Objectives

The goal of this work is to explore the role of biogeochemical cycles in the boundary layer and biosphere, and their effect on global atmospheric budget of source gases. This work will provide the framework for determining how rapid removal in the boundary layer changes the atmospheric lifetime and ozone depletion potential of source gases. The scope of the work involves investigating and reconciling the short lifetime implied by the extreme variability of the observed CH₃Br (methyl-bromide) concentration in the boundary layer and the much longer lifetime derived from known removal processes occurring in the free troposphere. Our plan is to quantify the problem by going through the following steps:

- Determine the rate of exchange between the free troposphere and the boundary layer for source gases.
- Quantify the rate of loss of source gases to the soil and vegetation at the bottom of the boundary layer. And use this information to estimate the fraction of source gases emitted at the ground that will reach the free troposphere, and the partial lifetime of the source gases in the free troposphere due to transport to the boundary layer.
- Explore the seasonal variability of source gases in the boundary layer.
- Identify the implications of 1, 2, and 3, in determining the lifetime and ozone depletion potential of the source gases. We will develop a methodology that is applicable to all sources gases in general, but will focus on methyl bromide as a specific example when calculations are performed.

Summary of Progress and Results

This contract was signed in June 1999. We have started the initial review of the treatments used to estimate the entrainment velocity at the top of the boundary layer. We will continue with the study and used a parameterized boundary layer model to examine the variation in the concentrations of a source gases in the boundary layer.

Publications

None

Use of SAGE II Data to Validate Results from the AER 2-D Aerosol Model

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Research Objectives

This contract, which began in June 1999, involves using SAGE II data to test, improve, and validate a two-dimensional model of atmospheric transport, chemistry, and microphysics with emphasis on periods with volcanic eruptions. Our participation in the SAGE II team has the following goals: (1) to conduct stratospheric aerosol modeling studies using a variety of 2-D transport formulations and making comparisons with SAGE II data taken during post volcanic activity periods; (2) to conduct data analysis of the temporal variation of optical depth and mass loading in the stratosphere during volcanic periods using various methodologies to estimate aerosol composition and size distributions; (3) to enhance the AER 2-D aerosol model with emphasis on circulations parameters, convection, expanded chemistry, and removal rates due to cloud processes; and (4) to extend the model studies and data analysis to the upper troposphere.

Summary of Progress and Results

Progress to date on this contract has included a number of significant model upgrades and some model calculations with comparisons to SAGE II and other data sets.

Model Upgrades: The AER 2-D sulfate aerosol model and the AER 2-D chemistry transport model (CTM) were operated as separate models, but have recently been combined into one model. In the past, operation as separate models required input of OH and O₃ to the sulfate model from the CTM and input of surface area density to the CTM from the sulfate model. With the models combined, perturbation calculations can be done with a single calculation rather than a series of two or more different calculations. While this currently has little effect on model results, it will allow for greater interactivity of sulfate and other trace gases in the future (such as effect of volcanic SO₂ on OH). For example, we could allow HNO₃ to condense onto sulfate aerosols and generate PSCs of STS composition. Other model updates which have been recently implemented are an increase in horizontal grid resolution from 9.5 degrees to 5 degrees and new cross-sections for SO₃ photolysis.

New Calculations Using Different Transport Rates: Transport remains a major model uncertainty in the calculation of stratospheric tracers and aerosol concentrations. 2-D models in general are known to have calculated age-of-air that is too young, suggesting that the transport

rates used in the models are too fast compared to the real atmosphere. In order to analyze the sensitivity of model results to transport rates, we have generated four new streamfunctions. A circulation we label "NCEP" was created using the 1982-1994 climatology of heating rates available on the "Reanalysis CD-ROM" published in the Bulletin of the AMS in 1996 [Kalnay *et al.*, 1996]. Three additional streamfunctions have been generated based on UARS data, with the radiative heating component calculated [Eluszkiewicz *et al.*, 1996, 1997] from 1992 MLS, 1993 MLS (version 5), and 1992 CLAES (version 7) O₃, H₂O, and temperature data. Below 100 mb, where UARS data does not exist, the heating rates from NCEP are used. We also make use of the transport circulation, both the streamfunction and eddy diffusion coefficients, of the GSFC 2-D model [Jackman *et al.*, 1996; Fleming *et al.*, 1999]. Age-of-air calculated using the NCEP streamfunction with GSFC diffusion coefficients generates age-of-air up to 6.5 years, while the MLS and CLAES streamfunctions generate age-of-air in the 3.5 to 4.5 year range. These different transport circulations are found to significantly improve calculated ozone in the lower midlatitude stratosphere relative to the standard AER transport. Mt. Pinatubo simulations have been performed with three different transport circulations, the AER, GSFC, and NCEP, from June 1991 to June 1995. All three show global aerosol burdens similar to SAGE II observations, with a return to background levels after about 3 years.

Comparisons of Model Results with Balloon Observations: Balloon observations of OCS at 35°N in September 1996, 65°N in July 1997, and 70°N in May 1997 are available from the MkIV instrument (Jeff Toon at JPL). Model-calculated OCS agrees well with the MkIV data using the AER, GSFC, and "NCEP" transport circulations. Model calculated SO₂ concentration at 28°N in April is compared with measurements by ATMOS in April 1985. The results calculated using different circulations do show significant differences in calculated SO₂, but the measurement uncertainty does not allow us to differentiate among the circulations.

Use of Aerosol Effective Radius as a Diagnostic for Pinatubo Aerosol Decay: Aerosol effective radius was calculated during the Pinatubo period for a point at 40°N and 18 km using the AER, GSFC, and NCEP transport circulations. For all circulations, the initial effective radius is 0.13 μm, decreases to 0.05 μm one month after the eruption, and then rises to ~0.45 μm by 12 month after the eruption. Starting at 12 months after the eruption, effective radius begins a slow decay, with the AER transport showing the most rapid decay. Four years after the eruption, aerosol effective radius is still elevated above background levels (0.18 μm for AER, 0.22 μm for GSFC, and 0.25 μm for NCEP) at 40°N and 18 km.

Publications

None

Assessing the Role of Coupling between Chemistry and Climate

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Research Objectives

The primary focus of our research is on studies of interactions between atmospheric chemistry, atmospheric composition and concerns about climate change, including studies of global scale tropospheric and stratospheric processes and the potential effects of natural perturbations and human related activities. Model development and applications are involved in this research.

Summary of Progress and Results

The publications below summarize the many accomplishments during the 1997-1999 period. In addition to the research projects resulting in journal articles and book chapters, and the IPCC, NAS, and WMO assessment work, we also had lead author responsibilities for the international intercomparison of stratospheric models under the NASA-sponsored Modeling and Measurements II, which is still in press. Because of space limitations, several publications were not included in the list below.

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Chemistry and Transport in a Multi-Dimensional Model

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Research Objectives

We focus on two primary scientific goals: the hydrological cycle of the stratosphere and the modeling of atmospheric chemistry and biogenic sources and sinks of methyl bromide. Our efforts are aimed at integrating new information obtained by spacecraft, shuttle and oceanic measurements to achieve a better understanding of the chemical and dynamical processes that are needed for realistic evaluations of human impact on the global environment. The major perturbations on the water in the stratosphere in the last decade are the secular increase of methane and the eruption of Pinatubo. One possibility is a change in the Brewer-Dobson circulation of the stratosphere, associated perhaps with global climate change. The Caltech/JPL multi-dimensional chemical transport model (CTM) photochemical model is used to simulate the effects of these perturbations of the stratosphere. The results are checked as to whether we have the correct understanding of the hydrological cycle and whether current photochemical models can reproduce the observed changes, of which the most puzzling are the trends in stratospheric humidity. The major datasets used for detailed comparison with model results include those obtained by the Stratosphere Aerosol and Gas Experiment (SAGE II), the Halogen Occultation Experiment (HALOE) and the Atmospheric Trace Molecular Spectroscopy (ATMOS). The second task is to initiate an in-depth examination of the atmospheric and oceanic budget methyl bromide (CH_3Br). The proposed research addresses some essential aspects of the coupling between the marine and terrestrial environments and the atmosphere that are poorly quantified at present for CH_3Br , whose regulation has recently been discussed at the highest levels of government. A major goal of the proposed research is to characterize sources, sinks, and distributions of CH_3Br , including coupled biological, chemical, and physical interactions. We use the Caltech/JPL CTM to pursue the following scientific objectives: (a) to characterize the latitudinal and seasonal distribution of CH_3Br ; (b) to identify (or constrain) the missing CH_3Br ; and (c) to assess the impact of global warming on the oceanic sources of CH_3Br .

Summary of Progress and Results

Using measurements of the isotopic composition of stratospheric water by the ATMOS instrument we inferred the convective history of stratospheric air. Convection is primarily responsible for transporting water vapor from the surface to the upper troposphere, where the water can either pass the tropopause as ice particles or be brought into the stratosphere via the Brewer-Dobson circulation. But the connection of water vapor transport to the stratosphere and convection has been clearly demonstrated in our work and may have implications for understanding the secular changes of water vapor in the stratosphere. Related work includes the study of CH₄ and H₂ using data from ATMOS to understand the budget of total hydrogen in the middle atmosphere. Our interest in the hydrological cycle motivated us to study the interannual variability of clouds in the TOMS (Total Ozone Mapping Spectrometer) reflectivity data. This project is an example of how a global data set that is primarily obtained for atmospheric composition (O₃) may be used for climate studies.

The other major theme of our research program is the interaction between the biosphere and the atmosphere. The biosphere influences the global environment (climate and the ozone layer) via trace gases, such as dimethyl sulfide and methyl halides.

Other related accomplishments include the study of isotopic fractionation of atmospheric species, e.g., N₂O and CO₂. Our theory suggests that we now have the ability to probe the middle atmosphere at a level of sensitivity where subtle details such as the isotopic composition of simple molecules can yield measurable systematic effects. This creates the possibility that one may probe the chemistry and dynamics of the middle atmosphere using all of the N₂O and CO₂ isotopomers. The N₂O and CO₂ isotopomers are virtually identical in chemistry so that the observed fractionation is a simple function of the aging of the air parcel.

Publications

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Organic Bromine in the Troposphere

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Research Objectives

The objectives of this study are threefold: (1) to develop a better understanding of the role that the oceans play in regulating the atmospheric concentrations of total organic bromine; (2) to constrain the tropospheric budget of total organic bromine; and (3) to assess the effect that perturbations in anthropogenic organic bromine emissions will have on the total atmospheric budget. These goals are being met through the compilation of a gridded ocean data set of saturation anomalies, production rates, and degradation rates for methyl bromide (CH_3Br), dibromomethane (CH_2Br_2), and bromoform (CHBr_3). This data is then used in a coupled ocean-atmosphere box model to predict the distribution of emission and uptake rates. The emission and uptake rates for these gases are used to constrain 2-D and 3-D atmospheric models. The models are run to test the sensitivity of the atmospheric concentrations to changes in the factors controlling the emission (both natural and anthropogenic) and uptake of these trace gases.

Summary of Progress and Results

Our CH_3Br ocean-atmosphere box model [Butler, 1994; Yvon and Butler, 1996] was modified to include CHBr_3 , dibromomethane CH_2Br_2 , dibromochloromethane (CHBr_2Cl), and bromodichloromethane (CHBrCl_2). The model was also modified to include biological degradation rate constants [Yvon-Lewis and Butler, 1997] and production rates for the calculation of emission and uptake rates.

Calibrations were obtained and applied to data from three past cruises (Bromine Latitudinal Air/Sea Transect I-III) for CHBr_3 and CH_2Br_2 . The CH_3Br data from these cruises was calibrated and published previously [Lobert *et al.*, 1995, 1996, 1997]. The combined data sets from these cruises span the latitudes 72°S to 52°N with data from the Southern Ocean, Eastern Pacific Ocean, and Central Atlantic Ocean. Many oceanic regimes were encountered on these cruises, however the data sets are still limited both temporally and spatially. In order to adequately

constrain a gridded ocean model coupled to a 3-D chemical transport model, it is necessary to have substantial latitudinal, longitudinal and seasonal data.

The results of measurements of CH₃Br, CHBr₃, and CH₂Br₂ made during a recent cruise in the North Atlantic were incorporated into the ocean data set. These data span the longitudes 12°W to 80°W, and the longitudinal transects were separated by 6 weeks. This data helps to fill in some of the spatial and temporal gaps in the earlier data sets. An area covered by one of the previous cruises was sampled during this cruise, which was at a different time of year, adding to the temporal coverage.

The minimum *in situ* gross production rates necessary to account for the observed net fluxes of these gases have been determined. These rates are being used to model the emission of these gases from the ocean independent of the uptake that is occurring simultaneously. The uptake rates have been determined from calculated chemical degradation rate constants and, in the case of CH₃Br, measured biological degradation rate constants. The factors (temperature, biological population, etc.) that control both the gross production rate and the degradation rate are likely to affect each process differently (e.g., increasing temperature will increase chemical degradation while it could reduce the biological degradation or increase the biological production). In order to complete objective 3, each process must be included in the model separately along with their respective dependencies.

We are currently using these data in conjunction with a 2-D model to examine the sensitivity of the atmospheric concentrations to the different processes controlling oceanic uptake and emission. The initial goal was to use a 3-D model for these tests, however due to the paucity of data for all of these gases, with the possible exception of methyl bromide, the extrapolation onto a global grid for a 3-D model is not yet recommended.

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Butler, J. H., J. W. Elkins, S. A. Montzka, T. M. Thompson, T. H. Swanson, A. D. Clarke, F. L. Moore, D. F. Hurst, P. A. Romashkin, S. A. Yvon-Lewis, J. M. Lobert, M. Dicorleto, G. S. Dutton, L. T. Lock, D. B. King, R. E. Dunn, E. A Ray, M. Pender, P. R. Wamsley, and C. M. Volk, 5. Nitrous Oxide and Halocompounds, in *Climate Monitoring and Diagnostics Laboratory Summary Report No. 24*, D. J. Hofmann, J. T. Peterson, and R. M. Rosson, (eds.), National Technical Information Services, Springfield, VA, 91-121, 1998.

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ASSESSMENT, COORDINATION, MISCELLANEOUS

Ocean Sources and Sinks of Trace Gases

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Research Objectives

The objective of this study is to improve our understanding of the processes responsible for the oceanic fluxes of atmospheric methyl bromide, to correlate the fluxes with satellite measurements such as temperature and windspeed, and, ultimately, to be able to predict the response of these oceanic fluxes to some global change, such as increasing temperature. By conducting concurrent measurements of the concentrations of methyl bromide in the air and water along with measurements of methyl bromide degradation (done by Dr. Eric Saltzman, University of Miami) and its biological production (Dr. Paty Matrai, Bigelow Laboratory for Ocean Sciences) we should be able to constrain the budget of methyl bromide in the surface ocean. By doing this in areas where good satellite coverage is available, we can then compare our findings with real-time measurements of critical oceanic properties and evaluate their predictive capabilities.

Summary of Progress and Results

We completed our initial field cruise in the Atlantic Ocean in May-June 1998 on *NOAA Ship Ronald Brown*, with James Butler serving as Chief Scientist for the cruise on Leg I and Shari Yvon-Lewis as Chief Scientist on Leg III. We have processed most of the data into a useful and presentable format for evaluation and we have presented results from this cruise at a special SeaWifs session at the 1998 Fall AGU meeting in San Francisco. Although the cruise was scheduled to involve work on three Legs in the Atlantic Ocean from 7 May through 7 July 1998, we took the opportunity to keep the instruments on board and running through 27 July, as the ship made a transit run from Miami to Portland, Oregon, via the Panama Canal. Dr. Daniel King from NOAA/CMDL stayed on board, along with volunteers from our associate institutions, to conduct the analyses and to maintain the instrumentation. The addition of this transit leg greatly enhanced our data set, allowing us to obtain measurements in waters where no measurements have been reported previously and allowing us to sample waters previously studied by ourselves

[Lobert *et al.*, 1995] and others [Singh *et al.*, 1983]. These overlaps, along with one overlap in the Atlantic [Butler *et al.*, 1995; Lobert *et al.*, 1996], will help us evaluate the possibility of seasonal driving forces in flux of CH₃Br from the surface ocean and will allow us to evaluate discrepancies among previously published data sets.

The second cruise is under way at this time, also on the *NOAA Ship Ronald Brown*. From 14 September through 23 October 1999, the cruise runs from Kwajalein Atoll at 8°N in the West Pacific, to Dutch Harbor, AK (Unalaska Is.) in the North Central Pacific, to Seattle in the Northeast Pacific, and involves the same participants and measurements as went on the first cruise. A guest scientist, Dr. Georgina Sturrock of CSIRO-Australia, is participating on the cruise as well.

Our remaining efforts will focus on finishing the second cruise, processing and finalizing data from both cruises, and compiling the data into a database with CH₃Br data from other NOAA/CMDL cruises (BLAST I, II, III). A data report will be prepared and we will begin working on manuscripts for publication. We anticipate meeting with our co-investigators on this project to evaluate our collective findings, to plan for dissemination and publication of results, and to discuss and plan the integration of these and other data into a global model of oceanic CH₃Br. The first round of manuscripts on the distribution, flux, production, and degradation of methyl bromide in the ocean is scheduled for submittal in November 1999.

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Data Survey and Evaluation

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Research Objectives

This task supports JPL participation in the NASA Panel for Data Evaluation. The purpose of the task is to maintain an updated set of evaluated rate constants and photochemical cross-sections for use in stratospheric modeling, and to publish the evaluated data in a form accessible to the community of atmospheric scientists.

Panel Members

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S. P. Sander, Chairman, Jet Propulsion Laboratory
R. R. Friedl, Jet Propulsion Laboratory
D. M. Golden, SRI International
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Summary of Progress and Results

Evaluation Number 12 was published in January 1997. A Panel meeting was held in June 1998, to begin preparation of an interim update of the evaluation. Recommendations for that update were finalized at a meeting in August 1999.

Publications

A series of eleven evaluations has been published since 1977, the most recent being Evaluation Number 12, December, 1997, JPL Publication 97-4.

SPARC Data Center

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Research Objectives

As part of the World Climate Research Programme (WCRP) the SPARC (Statospheric Processes And their Role in Climate) project aims to gain a better understanding of the effects of the stratosphere on climate. The objectives of the SPARC Data Center are to coordinate data exchanges between the members of the science community and to provide easy access to stratospheric data sets relevant to SPARC research. Data resources are available from numerous national organizations, such as NOAA, NASA, and NCAR, as well as universities and several international organizations. The SPARC Data Center's goal is to facilitate the investigation and retrieval of relevant data sets. This includes the establishment of a publicly accessible website, which links SPARC related information and data, gives access to reference data sets, and graphically displays analyzed data.

Summary of Progress and Results

The SPARC Data Center went into operation at the end of July 1999. To accommodate extensive data sets, a computer with a sizeable storage device was purchased. Within days, the SPARC Data Center went online. As a first step, the website set up links to Internet resources for the different SPARC projects.

Reference data sets based on UARS measurements and NCEP model analyses were then put online following demands from different SPARC members. On request from the SPARC gravity wave initiative, high-resolution temperature and wind data from radiosondes for 1998 were purchased from NOAA. These data are now available from the SPARC Data Center. Several SPARC members have retrieved data from the Data Center's website within the first months of operation.

The SPARC Data Center has completed its start-up phase. Additional data sets will be made online in the future on request from the members of the SPARC science community. The functionality of the SPARC Data Center is currently being expanded to provide graphical displays of analyzed data sets.

Publications

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Isotope Fractionation Studies

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Research Objectives

The objective of this research program is to develop a stable carbon isotopic approach to independently estimate the industrial fraction of the total methyl bromide source to the atmosphere. The viability of this new approach depends on our ability to determine the isotopic signatures of all the major methyl bromide sources and the fractionation factors associated with the methyl bromide sinks. The viability of the project also depends on our ability to measure the stable carbon isotopic composition of methyl bromide in atmospheric samples. Thus the specific objectives of this program are to quantify the isotopic signatures of the major source and sink terms, and to develop the technology to preconcentrate methyl bromide from roughly 50 liters of ambient air and measure its carbon isotopic composition.

Summary of Progress and Results

Samples of methyl bromide were obtained from each of the major manufacturers worldwide, and a survey of the carbon isotopic signature of industrial methyl bromide was completed. The mean carbon isotopic composition of industrial methyl bromide is very light at approximately -55 per mil. These measurements and a model for interpreting the isotopic signatures of methyl bromide in the atmosphere are in press in the Proceedings of the National Academy of Sciences [McCauley, DePaolo, and Goldstein, 1999].

We have worked extensively with Larry Miller and Ronald Oremland (U.S. Geological Survey), on a number of experiments to determine the Kinetic Isotope Effects (KIE) associated with oxidation of methyl bromide by the bacteria strain IMB-1, and associated with hydrolysis. We found large isotopic shifts under laboratory conditions; the resulting KIE for bacterial oxidation is on the order of 1.065 at 32°C. The KIE decreases significantly at lower temperatures. We also determined the hydrolysis KIE from our bacteria-free controls to be approximately 1.005 at 32°C. Once again, there is a significant temperature effect with lower KIEs at lower temperatures. We are currently measuring the KIE of CH₃Br consumption in fumigated soils, and the KIE associated with chloride ion exchange.

A preconcentration system for ambient atmospheric samples has been constructed according to our in house design, and we have determined that it will effectively trap the required amount of methyl bromide. Currently we are refining the preconcentration routine by testing the efficiency

of the preconcentrator at various combinations of concentration and flow rate. This preconcentration system will be interfaced with a Gas Chromatograph - Combustion - Isotope Ratio Mass Spectrometer (GC-C-IRMS) which we have used extensively for our tests on KIE associated with methyl bromide sinks (bacterial oxidation, hydrolysis, and chloride ion exchange - as described above).

Publications

McCauley, S. E., D. J. DePaolo, and A. H. Goldstein, An isotopic approach for understanding the CH₃Br budget of the atmosphere, *Proceedings of the National Academy of Sciences*, in press, 1999.

Chemical Kinetic Data Evaluation Activities in Support of the NASA Upper Atmosphere Research Program

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Research Objectives

To provide the reliable, evaluated reaction rate, photochemical, and thermodynamic database required as input data for large-scale modeling efforts, which provide the basis for our understanding of atmospheric chemistry.

Summary of Progress and Results

Both the principal investigator and the co-investigator have participated in the data evaluation activities of the NASA Panel for Data Evaluation. The principal investigator has the primary responsibility for the review and evaluation of the rate data for reactions of halogen-containing species. The co-investigator has the primary responsibility for updating and documenting the thermodynamic property tables for this panel. He has initiated also a section on aqueous-phase kinetics and thermodynamics, which is under consideration by the panel. Updated and reevaluated databases have been presented at meetings of the Data Panel.

The principal investigator also participated in the data evaluation activities of the IUPAC Commission on Chemical Kinetics, Subcommittee on Gas Kinetics Data Evaluation for Atmospheric Chemistry. He has served as principal liaison between these two panels.

Publications

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Meteorological Support Facility and Data Management

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Research Objectives

As part of the Ames Earth Science Project Office (ESPO), we maintain a meteorological satellite downlink and display system (MSDDS) which is supported by the Upper Atmosphere Research Program (UARP). This system acquires, processes and displays meteorological satellite data from all current meteorological satellites, including both NOAA Polar Orbiters (AVHRR instrument) and GOES and other geostationary satellites (GMS, Japan, Meteosat, Europe). This system is a modular, transportable system, which was purchased for and is used to support airborne field missions virtually anywhere on the globe. The system is comprised of two subsystems, a tracking system for the polar orbiters, which uses a 1.2 meter dish, and a fixed 3.5 meter dish for acquiring geostationary satellite data. The data from the system are used by project forecasters in mission planning, as well as for post mission analysis of the mission data.

Another component of the ESPO is the data management function, supported by the Atmospheric Chemistry and Analysis Program (ACMAP). Under the direction of Steve Gaines, we have written format standards for exchange of data from the various instruments and investigator groups. These standards, and particularly the file naming convention, have been updated in the last year to be Y2K compliant. We have also set up processes for submission and automatic checking of the data to assure compliance with the standards. The data exchange is implemented in the field by setting up a local area network (LAN) and providing a central data archive computer to which all science team members submit their data. Once on this central machine, all data from all of the instruments is available to the entire mission science team.

Summary of Progress and Results

The MSDDS was acquired in 1991. It has been deployed on every major UARP airborne field mission since that time. It was first used in Bangor, Maine in support of the second Airborne Arctic Stratospheric Expedition (AASE II) in 1991-1992. It has since been deployed to Christchurch, New Zealand for the ASHOE/MAESA mission, and most recently to Fairbanks, Alaska for POLARIS. It has been an important forecasting tool used by the mission forecasters in weather forecasting and flight mission planning. It is used to plot the aircraft flight tracks on

top of the satellite cloud imagery to help provide a meteorological context for the flights. It has also been used in detailed, post-mission analysis, providing important cloud and albedo data which are key to analyzing the radiative measurements taken on the aircraft.

The data exchange and archiving function of the ESPO has been employed for every UARP field mission starting in 1987 with the tropical Stratosphere Troposphere Exchange Project (STEP) in Darwin, Australia. In this past reporting period the ESPO has provided data management for the Stratospheric Tracers of Atmospheric Transport (STRAT), Tropical Ozone Transport Experiment, Vortex Ozone Transport Experiment (TOTE/VOTE), Observations from the Middle Stratosphere (OMS), Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS), and Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SONEX).

Publications

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NIST-JANAF Thermochemical Tables for Species of Importance to Atmospheric Chemistry

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Research Objectives

The goal of this activity is to provide accurate and consistent thermodynamic data (heat capacity, enthalpy, entropy, Gibbs energy function, and the formation properties) for a series of important atmospheric chemical species. The evaluation process involves:

- The compilation of annotated bibliographies containing the relevant references needed to obtain the thermodynamic properties of the species.
- The generation of tabular summaries of the pertinent information; extraction of the spectroscopic, structural, and thermodynamic data; recalculations and adjustments of the reported values, where necessary; and the determination of the final values to be used in the calculation of the thermodynamic tables.
- The computation of the thermodynamic tables; this is done by several techniques to establish the sensitivity of the calculations to the input data.
- The documentation of the tables.

Summary of Progress and Results

In the initial activities under this project, the thermodynamic properties of the halogen oxide species were evaluated for the fluorine oxides, the bromine oxides, and the iodine oxides. As part of the present activity, this information is being updated. Also, a bibliography has been compiled for the chlorine oxides and there has been a preliminary analysis of the data on these species.

The data on the thermodynamic properties of the HX(g) species (X = F, Cl, Br, and I) have been compiled, evaluated, and thermodynamic tables calculated and a manuscript written. It has been submitted to the *Journal of Physical and Chemical Reference Data* and is ready for final review.

The data on the thermodynamic properties of H₂O₂, H₂SO₄, and HNO₃ have been compiled, reviewed, and thermodynamic tables calculated. A manuscript covering these species has been written and submitted to the *Journal of Physical and Chemical Reference Data*.

The data on the thermodynamic properties of the carbonyl halides and related species have been compiled and reviewed and thermodynamic tables calculated. There are presently some questions about the details of the publication of these tables, including a possible expansion. We expect these matters to be resolved in the coming year.

A literature search has been completed on ozone and an evaluation of the thermodynamic data for this species will begin soon.

The evaluation of the thermodynamic properties of the Br/H/O and Br/N/O species has been started.

Publications

None

Development and Maintenance of the GEIA Web Site

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Research Objectives

The Global Emissions Inventory Activity (GEIA) is a major crosscutting activity of the International Global Atmospheric Chemistry (IGAC) Project, a core project of the International Geosphere-Biosphere Program. GEIA provides necessary emission inventories for comprehensive global assessments of past, present and future atmospheric chemistry, air quality and climate change. The GEIA Center, developed and operated by Dr. Paulette Middleton and her staff, coordinates GEIA planning efforts, develops and implements outreach strategies, and makes effective distribution of GEIA data bases and exchange of GEIA information possible through the NASA sponsored GEIA web site <http://blueskies.sprl.umich.edu/geia/>.

Summary of Progress and Results

The project tasks were:

- Manage the project and maintain liaison with the GEIA Coordinating Committee;
- Design and create Web pages describing GEIA projects and other information;
- Prepare and QA GEIA data bases and place them on the web site; and
- Create links to related web sites

These ongoing operational tasks were completed successfully. The GEIA Web Site has become the hub of GEIA information and data exchange because of the continued support of NASA. Expansion, maintenance, and updating of the GEIA web site will be supported through the GEIA Center operating budget. Requests for continuing support are being pursued through NASA and NSF.

Publications

The NASA sponsored GEIA web site activities have been reported at annual GEIA workshops and have been prominent in the recent GEIA 5-year plans. These summaries and other information all are available on the GEIA web site.

Biogeochemical Cycling of Halomethanes

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Research Objectives

Halomethanes include substances like CFCs, HCFCs, HFCs, and methylated halides, all of which have significant global-warming potentials (GWP) and/or ozone-degradation potentials (ODP). Some halocarbons arise from solely anthropogenic sources (e.g., CFCs) while others arise from a mixture of anthropogenic and biogenic sources (e.g., methyl halides). The tropospheric residence time of a halocarbon is a key factor in estimating its GWP or GDP. The major sink for most tropospheric halocarbons is reaction with hydroxyl radicals, and the kinetics of these reactions have been used almost exclusively to calculate GWP and GDP. However, some halocarbons can be degraded by diverse terrestrial and aquatic microbial communities, and in the case of substances like methyl bromide, the estimate of its tropospheric residence time has declined from 1.7 years (OH sink only) to <0.8 years (OH plus microbial/chemical oceanic plus terrestrial microbial sinks). Hence, the global atmospheric budget for MeBr is now out of balance, with identified sinks greatly exceeding identified sources. This project has focused primarily upon MeBr (although not exclusively) in attempts to understand the nature of the microbial reactions which constitute its terrestrial and soil sinks. We have isolated bacteria which grow on methyl halides and have found that these microorganisms can metabolize ambient tropospheric mixing ratios of this substance. In addition, we have discovered that a very large stable C isotopic fraction is achieved during bacterial oxidation of MeBr, resulting in ^{13}C -MeBr values of the residual, unoxidized MeBr that are enriched in ^{13}C by ~60 per mil. This work was done in collaboration with Dr. A. Goldstein at University of California, Berkeley. In another collaboration with scientists in the UK, we have found that the enzyme responsible for this fractionation is a cobamide-containing methyltransferase. Our results suggest that ^{13}C -MeBr values may prove to be important tools in identifying global sources and sinks for tropospheric MeBr.

Summary of Progress and Results

Methane-oxidizing bacteria represent important biotic sinks not only for methane, but potentially for a number of halocarbons as well. Previous studies, however, applied indiscriminate levels of HCFCs to cultures and soil. We hypothesized that these levels may have been inhibitory to methanotrophs and have now shown that HCFC-21 and HCFC-22 are competitive inhibitors of both particulate and soluble methane monooxygenase [Matheson *et al.*, 1997]. As a spin off of this study, we discovered that difluoromethane works well as a specific inhibitor of

methanotrophic bacteria [Miller *et al.*, 1998]. With regard to brominated methanes, degradation of MeBr, bromoform and dibromomethane could be observed in enrichment cultures obtained from the marine environment [Goodwin *et al.*, 1997]. Concurrently, we devised *in situ* techniques to measure ¹⁴C-MeBr oxidation in stratified Mono Lake water [Connell *et al.*, 1997]. Results suggested that methylotrophic bacteria rather than methanotrophs were responsible for the bulk of the MeBr oxidation. This was a highly significant finding which guided many of the aspects of subsequent work. Follow-up work on Mono Lake was published by Joye *et al.* [1999].

We next conducted a broad survey of natural waters (fresh, estuarine, marine, and hypersaline/alkaline) to determine if MeBr and dibromomethane were degraded by the naturally-occurring microbial flora [Goodwin *et al.*, 1998]. Activity was found in all 4 environments, with methanotrophs suggested as being important only in freshwaters while methylotrophs predominated in all the saline locales. Oxidation of dibromomethane was a significant sink with respect to its half-life in all 4 while for MeBr this was only significant in freshwater. A marine bacterium (strain MB2) was isolated which grew on MeBr and other methyl halides. With regard to soils, oxidation of ¹⁴C-MeBr was found to occur during field fumigation events [Miller *et al.*, 1997]. We were able to determine that facultative methylotrophic bacteria were responsible for this activity, and isolated strain IMB-1. Strain IMB-1 was further characterized in subsequent studies [Connell Hancock *et al.*, 1998; Schaefer and Oremland, 1999]. The organism is currently being applied to soils under field fumigation conditions in an attempt to reduce or eliminate outflux of MeBr to the atmosphere, and results are highly promising [Miller *et al.*, 1998].

Recent work has been conducted using strains IMB-1 and MB2 to follow stable C isotope fractionation associated with bacterial oxidation of MeBr, MeCl, and MeI. All 3 methyl halides undergo highly significant fractionation, achieving final ¹³C-methyl halide values enriched in ¹³C by as much as 60 per mil [Miller *et al.*, 1999]. The methyl halide transferase enzyme has been isolated and a comparable fractionation has been determined. The above work represented collaborations with the labs of Prof. A. Goldstein (University of California, Berkeley) and Prof. D. Harper (University of Belfast). In a collaboration with Dr. P. Crill, we have found that strain IMB-1 will oxidize MeBr at its ambient tropospheric mixing levels [Goodwin *et al.*, 1999]. Thus the work with stable C isotopes is relevant to *in situ* conditions.

Publications

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